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ROLES OF KINETIC AND POTENTIAL ENERGIES IN CONJUGATION II.* ANILINE AND NITROBENZENE

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An analysis of the energy components of the conjugation energy between the substituent and the phenyl group in aniline and nitrobenzene showed that there are two types of conjugation: the conjugation energy in aniline, with an electron-donating substituent, is given by the decrease in the kinetic energy of electrons, whereas that in nitrobenzene, with an electron-withdrawing substituent, is caused by the decrease in the potential energy. Physical interpretations are given of the arrows in the organic electron theory of these compounds.

Conjugation is associated with energetic stabilization in the π-electron system. The fundamental energies which govern a system are electrostatic potentials (between electrons, between an electron and a nucleus and between nuclei) and kinetic energies of nuclei and electrons and in a balance given by the virial theorem. Since nuclear motion can be treated separately,[2] the major and important energies in this study were the potential energy (V) and the kinetic energy of electrons (T). We considered that conjugation can be interpreted in such energy terms.

Based on the above idea, in Part I[1] we studied the process of conjugation in vinylamine and nitroethene as prototypes of the conjugation between a π system and an electron-donating or -withdrawing substituent. The conclusion was that there were two different modes of conjugation: the conjugative stability given by a decrease in the kinetic energy of electrons and that given by a decrease in the potential energy, which could be termed *the conjugations of the kinetic energy origin and the potential energy origin*, respectively. The conjugative stability in vinylamine is produced by an excess decrease in the kinetic energy over the increase in the potential energy (the 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 that belonging to the nitro group (the potential energy origin). Here a further question is whether or not these findings are valid for benzene derivatives. The marked difference in the π systems between the vinyl and phenyl groups is in that the latter has an aromatic stabilization energy.

EXPERIMENTAL

Energy component calculation. In the Hartree–Fock MO theory, the Fock operator is composed of the sum of the operators associated with the kinetic energy of an electron, the potential energy of an electron in the field of nuclear charges and the repulsion energy between electrons. The electronic energy (E^{el}) of a molecule is hence divided into the kinetic energy of electrons (E^T) and electronic potential energy. The latter is further divided into an attractive one-electron potential (E^V) and repulsive two-electron (E^J) energies. They are calculated by the following equations:

$$E^T = \sum_{r,s} P_{rs} T_{rs} \qquad (1)$$

$$E^V = \sum_{r,s} P_{rs} V_{rs} \qquad (2)$$

$$E^J = 1/2 \sum_{r,s} P_{rs}(F_{rs} - T_{rs} - V_{rs}) \qquad (3)$$

where P_{rs}, T_{rs}, V_{rs} and F_{rs} are the density, kinetic energy, one-electron potential energy and Fock matrix elements, respectively, between atomic orbitals r and s. The summation may run over all atomic orbitals. The potential (V) and kinetic energies (T) are thus, given by

$$V = E^V + E^J + \sum_{A>B} E^N_{AB} \qquad (4)$$

$$T = E^T \qquad (5)$$

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where E_{AB}^N is the nuclear repulsion energy between atoms A and B and the summation may run over all atoms without duplication.

In the LCAO MO theory, each MO is expanded by a linear combination of atomic orbitals, and via the Fock matrix the three- and four-centre integrals of two-electron integrals can be reduced to two-centre terms. Hence both the total (E) and the component energies are formally expressed by the sum of monocentric (E_A) and bicentric (E_{AB}) terms. Following the method presented in the definition of Mulliken population analysis,[3] the kinetic and potential energies with respect to the electrons belonging to a specific atom, X, $T(X)$ and $V(X)$ are defined as

$$V(X) = E_X^V + E_X^J + 1/2 \sum_{X \neq A} (E_{XA}^J + E_{XA}^V + E_{XA}^N) \quad (6)$$

and

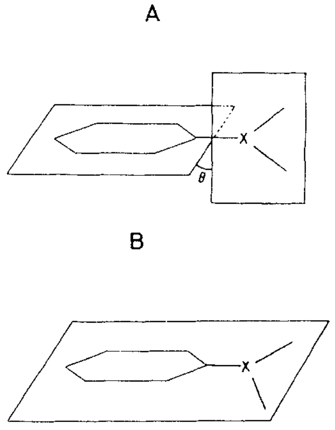
$$T(X) = E_X^T + 1/2 \sum_{X \neq A} E_{XA}^T \quad (7)$$

Since the wavefunction is expressed by the Slater determinant with the elements of molecular orbitals (MOs: ψ_i) and since π MOs do not mix with σ MOs in a planar π-conjugated system, E^{el} and its component energies in a conjugative structure can also be expressed as the sum of π- and σ-electron energies.[4] Details of the calculation may be found elsewhere.[4-7]

The above technique has some fundamental difficulties. The partitioned energies are dependent on the size of the system and the basis set of the MO method.[8] Therefore, one cannot compare the E^X values (where X = T, V and J) in different systems and in different basis sets. To avoid such difficulties, the partitioned energies should be compared only in the same system and the same basis set in addition to the requirement that the basis set must be carefully chosen.

We have already studied the basis set dependence of energy components and found that the 4–31G[9] and 6–31G[10] basis sets give the fairly reasonable results.[11] Therefore, we adopted 4–31G in this study. The components of the total energy were shown to be sensitively affected by the threshold of geometry optimization.[11] The convergence at the density matrix in the SCF iteration is also another important condition which affects the energy components, we adopted the thresholds of 0·00075 (maximum) and 0·00005 (rms) hartree/bohr or rad for geometry optimization, which is less than one fifth in the standard optimization and 10^{-10} of the SCF tolerance at the density matrix, which is 1000 times severer than the standard SCF criterion (10^{-7}).[11] We used the GAUSSIAN-80H program [a Hitac version of the GAUSSIAN-80 program (QCPE 437, 1982)] at the Computer Center in the University of Tokyo. [In the study of prototypes by 6–311G** (for the 6–311G** basis set, see Ref. 12), we adopted a much severer threshold [0·00003 (maximum) and 0·00002 (rms) (hartree/bohr or rad); the present thresholds are the practical compromises given in Ref. 11].

Method of analysis. We examined aniline ($C_6H_5NH_2$) as a benzene derivative with a typical electron-donating substituent and nitrobenzene ($C_6H_5NO_2$) as one with a typical electron-withdrawing substituent. Those compounds are known to have a planar or near-planar geometry as the most stable conformation.[13-16] Such planarity may be the result of conjugation. If there were no conjugation between the phenyl group and the substituent, the orthogonal structure would be the most stable conformation because such a structure has the least interatomic repulsions (steric effect). We therefore employed the optimized orthogonal structure (A) as the reactant structure for the conjugation (Schemes 1 & 2).



Scheme 1

$$\begin{tikzcd}
A \arrow[r] \arrow[dr, phantom, "\leftarrow \text{optimization} \rightarrow"] & B' \arrow[d] \\
A' \arrow[u] & B \arrow[l]
\end{tikzcd}$$

A: geometry-optimized orthogonal structure

B: geometry-optimized planar structure

Scheme 2

The total energy of any stationary system consists of T and V in a balance determined by the virial ratio ($V/T = -2$). The balance is broken in the chemical process because the change of either T or V exceeds that of the other. Our method is to examine this imbalance.

Consider the process when A becomes the planar structure (B) through the minimum energy path. As the angle of the planes between the phenyl group and the functional group (θ) decreases to zero, the bond length between the carbon and nitrogen atoms and the geometries around the functional group may be changed. Since angular coordinates do not contribute to the virial relationship,[17] the equation

$$V = -2T \tag{8}$$

holds exactly in this process.

The geometrical change on the minimum energy path takes place as the result of the conjugation, which consists of three primary effects: the change in interatomic distances, the loss of hyperconjugation and the formation of π bonds between the phenyl and functional groups, each of which involves an energetic change. It should be noted that *in order to study the cause of the conjugation, one must eliminate the effects caused by the geometrical changes*. To this end we considered a planar intermediate structure (B′) for which all geometrical parameters were the same as those in A except θ, which is the same value as in *B*, usually zero. With this structure the virial theorem [Eqn(8)] no longer holds; elimination of the geometrical effect causes an imbalance in the virial relationship, which we carefully analysed. The energy difference between A and B′ is produced by the π conjugation and that between B′ and B corresponds to the energy caused by the geometrical change due to the conjugation.

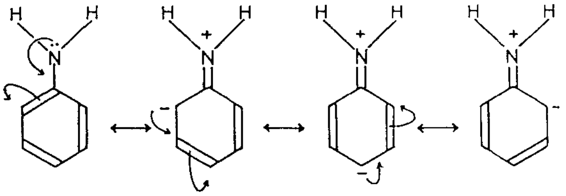
We also considered the process in which the optimized conjugative structure (B) was changed without optimization, to the orthogonal structure (A′) by simple rotation of the substituent; the energy change between B and A′ corresponds to the broken conjugation. With the orthogonal structure, the π conjugation is broken and may be replaced by a weak hyperconjugation. The energy at the orthogonal structure includes the effect of such a hyperconjugation.

RESULTS AND DISCUSSION

Aniline

The optimized geometries of aniline and nitrobenzene in both A and B conformations are shown in Table 1. In accordance with reported observations,[13,14] the two hydrogen atoms of the NH_2 groups are located slightly out of the molecular plane.

MO calculations[18] and measurements of dipole moments[13,14] showed that the lone pair of electrons on the nitrogen atom of the substituent flows to the phenyl group. The conjugation in aniline is expressed in organic chemistry as shown in Scheme 3, which explains well the chemical nature of aniline. Here the question was, "Why do the electrons on the atom with a high electronegativity flow to the carbon atoms with a low electronegativity?" The answers to this question have not yet been elucidated, although the MO interaction between the phenyl group and its substituent has been studied in many cases.[18] Probable answers are that the lone pair of electrons delocalizes (1) to release their own interelectronic repulsion and (2) to release the kinetic energy pressure of the lone pair of electrons (since without conjugation the lone pair of electrons must localize itself in a small region of the atomic orbital, resulting in a high kinetic energy).



Scheme 3

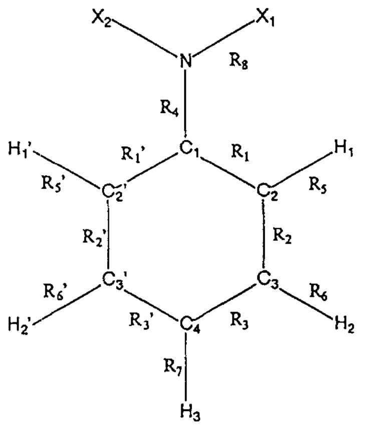
On changing from A to B′, the total energy is decreased. Such a stabilization is produced by conjugation between the two functional groups. The changes in energy components are important; the potential energy increases while the kinetic energy decreases. The change in the kinetic energy is much larger than that in the potential energy, causing the total energy to be lower. Hence the decrease in the kinetic energy is the source of the conjugation stability.

Since the geometries for both A and B are optimized with respect to the respective total energies, the energy change between A and B (Figure 1) must satisfy the virial theorem of difference, $\Delta T = -\Delta V/2$, where ΔT and ΔV are the differences between two conformations. Comparison of B′ with B reveals that although optimization of all geometrical parameters does not produce a large amount of total energy, its components encounter drastic changes: the potential energy drops by 195 kJ mol^{-1} while the kinetic energy rises by 188 kJ mol^{-1}, resulting in the virial theorem of difference between A and B being reasonably satisfied.

The process B → A′ is the case when the conjugation between the substituent and the phenyl group is disrupted. The total and kinetic energies increase while the potential energy decreases, indicating that the kinetic energy favours prevention of the conjugation from being broken.

We then examined the energy change on each atom. As shown in Table 2, the electron densities on N, C-1, C-3 and C-3′ are reduced by conjugation. In contrast, those on C-2, C-2′ and C-4 are increased, indicating the *ortho/para* orientation of the substituent. The kinetic energy on the N atom is substantially lowered by the process A → B′, i.e. the kinetic energy pressure on the N atoms is released by conjugation. This supports the conclusion that the release of the kinetic energy pressure on N is responsible for conjugation.

Table 1. Optimized geometries of A and B conformations (4–31G)



	Aniline (X = H)		Nitrobenzene (X = O)[a]	
Parameter	A	B	A	B
Bond lengths (Å)				
R_1	1·3853	1·3298	1·3754	1·3806
$R_{1'}$	1·3873	1·3928		
R_2	1·3833	1·3803	1·3825	1·3803
$R_{2'}$	1·3832	1·3803		
R_3	1·3834	1·3835	1·3837	1·3846
$R_{3'}$	1·3834	1·3836		
R_4	1·4254	1·3779	1·4572	1·4466
R_5	1·0705	1·0730	1·0704	1·0678
$R_{5'}$	1·0728	1·0730		
R_6	1·0720	1·0726	1·0704	1·0703
$R_{6'}$	1·0721	1·0726		
R_7	1·0720	1·0710	1·0710	1·0713
R_8	0·9938	0·9884	1·2206	1·2240
Bond angles (°)				
$\angle C_1C_2C_3$	120·57	120·45	118·39	118·66
$\angle C_1C_{2'}C_{3'}$	118·00	120·43		
$\angle C_2C_3C_4$	120·12	120·91	120·11	120·06
$\angle C_{2'}C_{3'}C_4$	120·05	120·90		
$\angle C_3C_4C_{3'}$	119·69	118·75	120·68	120·43
$\angle C_2C_1C_{2'}$	121·58	118·56	120·68	122·13
$\angle NC_1C_2$	119·14	120·73	118·66	118·04
$\angle C_1C_2H_1$	118·37	119·49	120·45	119·84
$\angle C_1C_{2'}H_{1'}$	122·08	119·49		
$\angle C_{2C3}H_2$	119·84	119·15	119·63	119·67
$\angle C_2C_{3'}H_{2'}$	119·87	119·17		
$\angle C_{3'}C_4H_3$	120·18	120·63	119·84	119·78
$\angle C_1NX_1$	144·84	121·07	117·61	118·22
Twist angles (°)[b]				
$\angle X_1NC_1C_{2'}$	−72·59	−0·00	90·00	0·00
$\angle X_2NC_1C_2$	72·59	180·00	−90·00	180·00

[a] Symmetry: C_{2v}.

[b] Counterclockwise twist angle around the C—N bond to the molecular plane.

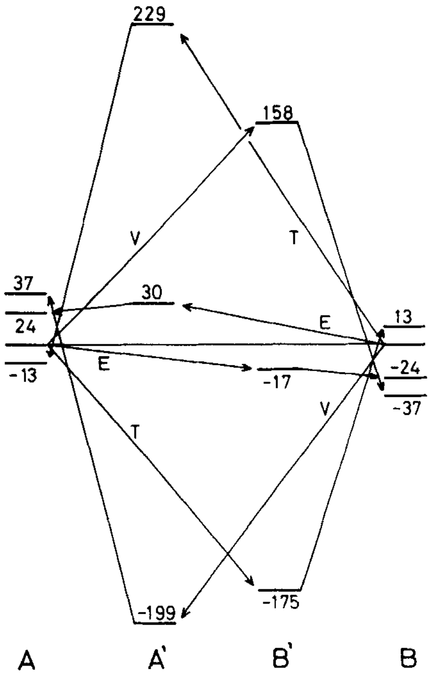
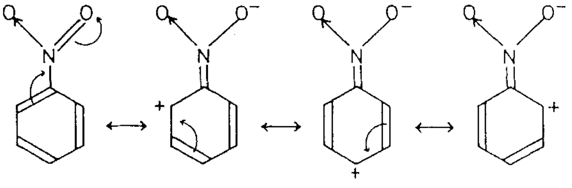


Figure 1. Changes in the total (E), kinetic (T) and potential (V) energies (kJ mol^{-1}) as the conformation changes from A to B and from B to A in aniline

Nitrobenzene

The nitrogen atom in nitrobenzene has been determined by both calculation and experiment to have a planar conformation.[15,16] Scheme 4 shows the organic-chemical expression of the conjugation in nitrobenzene, which suggests that the π electrons in the phenyl group move to the nitro group and are localized there. The MO theoretical calculations and the measured dipole moments[16,18] agree with such an organic-chemical expression.



Scheme 4

The energy changes in nitrobenzene, which are displayed in Figure 2, show a sharp contrast to the case with aniline: with the planar structure, the potential energy is lower and the kinetic energy is higher than those for the orthogonal structure. The change in the potential energy exceeds that in the kinetic energy.

Hence the conjugation stability is produced by a decrease in the potential energy. The energetic changes for the process B → A′ also indicate that the potential energy prevents the conjugation from being broken.

The changes in the electron densities and the partitioned energies in the process A → B′ correspond to the situation that the electrons in the phenyl group, especially those at C-4, move to the oxygen atoms of the nitro groups and that such a migration is caused by a lowering of the potential energy at the oxygen atoms. An increase in the electron density at C-1 is interpreted as the allylic position to the two oxygen atoms, which have two and three lone pairs of electrons. Those results are in agreement with the organic chemical-expression.

Change in π kinetic energy

The resonance energy in unsaturated hydrocarbons has been shown to be related to the π kinetic energy of electrons in the system.[4] Substituent effects in benzene derivatives are also interpreted in terms of conjugation in the π electron systems, where essentially no σ electrons are considered. It is therefore desirable to explain the substituent effect in terms of the π-electron energies only.

With a planar structure, the energies for the π electrons can be treated separately from the σ energies. The orthogonal structure completely breaks the π conjugation between the substituent and the phenyl groups. Instead, however, hyperconjugation takes place, making it difficult to handle the pure π electron energy. Therefore, we treated the case when the distance, R, between the phenyl group and the substituent is stretched from 1·3 to 2·4 Å with the planar conformations being retained.

Figure 3 shows the changes in the π kinetic energies as functions of R. The lines A and D represent the total

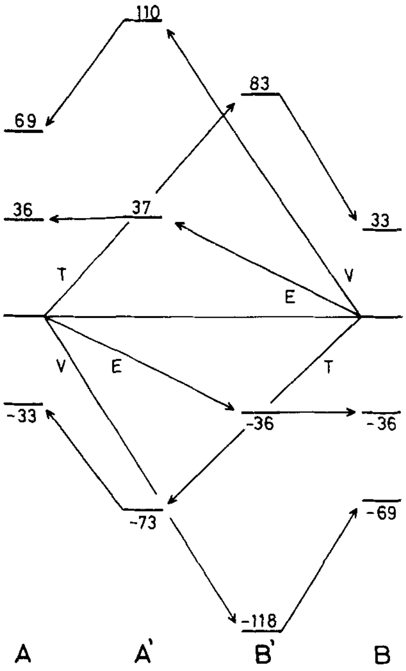


Figure 2. Changes in the total (E), kinetic (T) and potential (V) energies (kJ mol^{-1}) as the conformation changes from A to B and from B to A in nitrobenzene

Table 2. Electron density, kinetic energy and potential energy on atom in an orthogonal conformation (A) and their differences from a planar conformation (B′) by 4–31G

		Electron density		Kinetic energy		Potential energy	
Compound	Atom	A	Difference[a]	A[b]	Difference[c]	A[b]	Difference[c]
Aniline	N	7·9060	−11·0	55·684364	−2884	−114·311307	−98
	C_1	5·8199	−98·3	37·722858	−91	−74·325963	1795
	C_2	6·1568	64·7	37·888140	63	−76·504265	−1182
	$C_{2'}$	6·1781	41·5	37·903598	−12	−76·653488	−649
	C_3	6·1923	−26·3	37·881380	−91	−76·723785	574
	$C_{3'}$	6·1914	−25·0	37·876084	−73	−76·707479	493
	C_4	6·1886	28·3	37·873689	34	−76·656360	−378
Nitrobenzene	O	8·3747	21·3	74·817790	−17	−108·019134	−362
	N	6·7946	−29·7	54·393404	17	−151·798898	59
	C_1	5·7754	32·3	37·854483	−19	−73·656430	211
	C_2	6·1245	−1·3	37·747614	−7	−76·430838	29
	C_3	6·1925	14·0	37·869993	2	−76·965416	9
	C_4	6·1699	−15·7	37·867525	−7	−76·739853	3

[a] $D(B') - D(A)$ in 10^{-3} electron unit.

[b] In Hartrees.

[c] $X(B') - X(A)$ in kJ mol^{-1}, where X is the kinetic or potential energy.

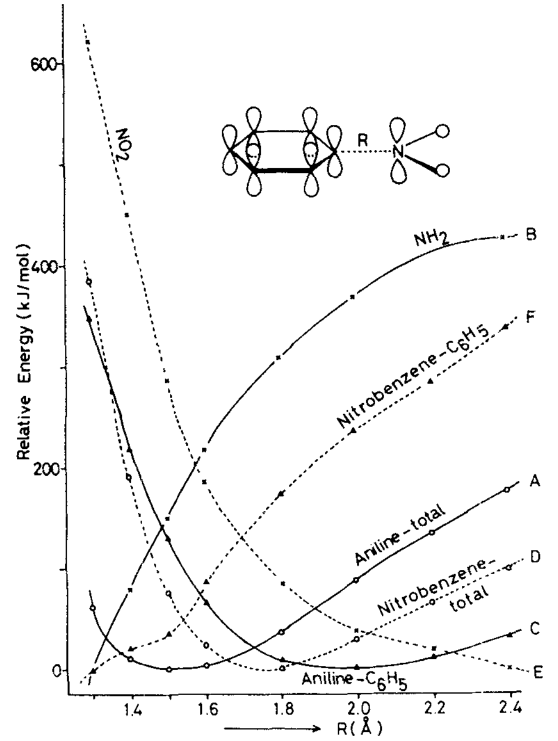


Figure 3. Changes in π kinetic energies as functions of R, the distance between the phenyl group and the substituent by 4–31G. The lines A and D represent the total kinetic energies and while B,C and E,F represent the kinetic energies of the substituents (B and E) and the phenyl groups (C and F) in aniline and nitrobenzene, respectively

π kinetic energies and B,E and C,F represent the π kinetic energies of the substituents (B and E) and the phenyl group (C and F) in aniline and nitrobenzene, respectively.

From these curves, if we consider the way that the NH_2 group approaches to the phenyl group, in aniline as R becomes shorter, the π kinetic energy of NH_2 becomes lower whereas that of C_6H_5 becomes higher. However, the decrease exceeds the increase and consequently the total kinetic energy decreases until $R = 1 \cdot 5$ Å. The kinetic energy decrease in NH_2 and the increase in C_6H_5 can be interpreted as being caused by the kinetic energy release in NH_2 and the increase in the π electrons in C_6H_5, respectively.

The changes in the π kinetic energy in nitrobenzene appear to be smaller but more complicated than those in aniline. The total kinetic energy shows a minimum at $R = 1 \cdot 75$ Å, which is far longer than the optimized distance ($R = 1 \cdot 4$ Å). The substituent portion increases while the π kinetic energy of the phenyl group continuously decreases, indicating that as R becomes shorter the π electrons on the phenyl group flow into the NO_2 group, causing a high kinetic energy owing to localization of the electrons on NO_2.

CONCLUSION

The results on the conjugation between the phenyl groups and its substituent are similar to those for the ethylene derivatives.[1] There are two different types of conjugation. In a benzene derivative with an electron-donating substituent, the conjugation causes the delocalization of the electrons on the substituent to the benzene π system to release the kinetic energy pressure of a lone pair of electrons (*kinetic-energy origin*) [the kinetic energy or kinetic energy pressure is easily related to the uncertainty principle (see Refs 19 and 20)]. On the other hand, conjugation of the π system with an electron-withdrawing substituent lowers the potential energy of the substituent (*potential-energy origin*).

The conjugations that we studied here are the typical cases which represent substituents with electron-donating and -withdrawing characteristics. However, other substituents may not be so delineated and may possess both electron-donating and -withdrawing characteristics. A detailed study of such compounds will require the precise determination of the potential and kinetic energies, perhaps using a method that exceeds the level of the Hartree–Fock theory.

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