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π-Conjugation in Y-Shaped Configuration. Does a Special Stability Exist?[1)]

Tomohiko Ohwada,† Hirotaka Kagawa, and Hiroshi Ichikawa*

Hoshi College of Pharmacy, Shinagawa, Tokyo, 143

†Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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The constrained HF method was applied to the estimation of conjugation of Y-shaped molecules. This method does not include the effect of the geometrical change, and gives a direct measurement of π-conjugation energy. We conclude that the magnitude of conjugation in a trimethylen–methane dianion is around that of a hexadienediide dianion, far less than that of a neutral cyclic aromatic compound (typically that of benzene). This is consistent with the previous conclusions obtained with the different energetic criteria. The physical meaning of Y-conjugation was interpreted in terms of relaxation of the kinetic-energy pressure of the π electrons.

Formation and stability of Y-shaped ionic species such as the trimethylen–methane (TMM) dianion **1** have been relevant to the question whether or not they have a special stability owing to the Y-shaped configuration.[2—20)] This is termed a 'Y-conjugation' or 'Y-aromaticity' issue, which was for the first time considered to the case of the extremely stable guanidinium cation **2**.[2)] There have been repeated experimental and theoretical discussions for[2,5,6,8,9)] and against[7,10,13,20)] Y-aromaticity of the TMM dianion (**1**) and the guanidinium cation (**2**) so far. Two energetic criteria to evaluate conjugative stabilization of the Y-shaped species have been put forward. One is comparison of the Y-shaped TMM dianion with a linear counterpart, *E*-/*Z*-butenediide dianions, the former being more stable than the latter, which is interpreted in terms of enhanced stabilization of the TMM dianion.[12,14,16—18)] The other is the energetical change arising from rotations of the peripheral groups (a methylene group in the case of the TMM dianion;[4)] an amino group in the case of the guanidinium cation[10)]) of the planar conjugating geometries to the perpendicular 'nonconjugating' geometries.[21)] Although the magnitude of the energy change upon rotation varies, depending on the approximations, the general trend is similar: the first rotation of the peripheral group of the planar ion raises the energy of the whole system, but in much smaller magnitude than the second and third rotations of the peripheral groups.[22)] In this context, special additional stabilization of the Y-shape molecules is lacking, because the first rotation would be more resistant if there were an 'aromatic-like' nature.

Recently Wiberg et al.[11)] discussed the origin of the stabilization of the TMM dianion in terms of plausible charge alternation (**1d**) which leads to internal Coulombic stabilization of the ion.[9)] They disagreed with this charge alternation mechanism as far as the TMM dianion is concerned because the central carbon atom has a fractional positive charge. Frenking et al. also used ab initio calculations to predict that the equilibrium geometries of the TMM dianion[13,16)] and the guanidinium cation[19)] are nonplanar, i.e., pyramidalized propeller-like structures, with respect to the rotation axis. They concluded that the special stabilization (i.e., Y-aromaticity) arising from the Y-shaped motif is absent; however, the energy difference between the pyramidalized and planar structures is very small.

Although there are some recent elaborations of the theoretical evaluation of the conjugation of the Y-shaped species,[11—20)] these works are still in accord with the above two energetic criteria. These criteria have essential limitations: The former energetic comparison method between the Y-shaped ion and the linear counterpart encounters difficulty in applicability, because the corresponding linear species of the guanidinium cation is not available. Thus, the systematic comparison of a variety of Y-shaped species by the energetic comparison method is impractical. Furthermore, in the rotation method the approximation of the rotational energy as π conjugation energy is, though intuitive for chemists, apparently problematic in two respects: (1) because rotation involves geometrical changes, the energy change upon rotation is the result of the changes both by the nuclear displacements and by the breakage of conjugation;[23)] (2) geometrical changes also involve σ–π orbital mixing, which precludes the assignment. Thus, these difficulties of the rotation method create ambiguity in the meaning of the energy change on rotation.

In this paper we will describe the estimation of the Y-conjugative stabilization of the TMM dianion and the guanidinium cation by using the recently developed constrained Hartree–Fock (HF) method, which provides the π-conjugation energy without any geometrical change.[24,25)]

Theories

Constrained Hartree–Fock Equation. To investigate the relationship between the π-electronic structure and its energy, one needs a method to determine the molecular energy as a function of the electronic structure. The constrained Hartree–Fock (HF) equation is one of the methods. This equation was first introduced by Mukherji and Karplus in 1963 to molecular quantum mechanics.[26] The purpose of these authors was to obtain the wave function that is constrained to give the known theoretical or experimental expectation values of operators rather than the total energy. The method was generalized by Brown,[27] and was applied to the SCF theory by Björnå in the early 1970s in order to obtain accurate expectation values of some physical properties.[28]

As described in our previous paper,[24] we found that the total energy of a non-conjugating electronic structure without any geometrical change can be obtained by applying this equation, wherein the constraints in the operator cancel the delocalization of the π electrons of specified interactions. The equation is,

$$(F+\lambda)C=\varepsilon' SC.$$

Herein F, C, and S are matrices of the Fock operator, molecular orbital (MO : ψ) coefficients, and overlap integrals, respectively, while ε' is the fictitious orbital energy associated with ψ. The parametric matrix, λ, constrains the electron distribution to be controlled. The bond-order ($P_{\mathrm{rs}}=2\sum C_{\mathrm{r}}^{i} C_{\mathrm{s}}^{i}$) between atomic orbitals (AOs) r and s is a function of λ_{rs}, an element of λ, where the λ_{rs} value is so determined that P_{rs} is nullified to cancel the delocalization between AOs *r* and *s*. The equation also gives the total energy and its components (kinetic/potential components and π/σ components)[29] as functions of P_{rs}. Thus, the difference (ΔE) in the total energies of the constrained and unconstrained wave functions defines the π conjugation energy. The detail of derivation has been described elsewhere.[24] Minimal basis sets were used in the calculations.

Results and Discussion

Conjugation of Y-versus Linear Dianions. The conjugation energy of the Y-shaped TMM dianion is evaluated by the constrained HF method as 102 kJ mol^{-1} and 267 kJ mol^{-1} due to a single (**1A**) and double (**1B**) cancellation of the anion conjugation (i.e., the energy change by the second constraint is the difference 165 kJ mol^{-1}) (Table 1 and Fig. 1).[30] On the other hand, the linear E-butenediide dianion **3** gives the corresponding energies as 21 kJ mol^{-1} (a single constraint (**3A**) on one of the terminal C–C bonds of **3**) and 72 kJ mol^{-1} (double constraints (**3B**) on both of the terminal C–C bonds), respectively. In the case of *Z*-butenediide dianion **4**, a single and double constraints gave the energy change of 24 kJ mol^{-1} (**4A**) and 85 kJ mol^{-1} (**4B**), respectively. Thus, the conjugation energy of the TMM dianion is definitely larger than those of the butenediide dianions, indicating the configuration-dependent conjugation. However, this energetic preference can be interpreted in terms of the intrinsic inhibition of the conjugation of the linear butenediide dianions rather than the highly enhanced conjugation of the TMM dianion. Conjugation in the anionic species is generally enhanced more than in neutral systems, as exemplified in the case of the allyl anion (the single constraint raised the energy as 203 kJ mol^{-1}).[30] The conjugation energies of the butenediide dianions are much less than that of the allyl anion. Rather, these energies are comparable to the conjugation energy of the neutral butadiene unit (–CH=CH–CH=CH–) (22 kJ mol^{-1}),[24] which is known to be one of the weakest conjugations. These extremely small conjugation energies of the butenediide dianions are reasonably interpreted in terms of the conventional resonance structure of the linear dianions: a resonance structure (**3b** or **4b**) involving adjacent carbanion centers will not contribute significantly. The bond orders of the terminal C–C bonds (Table 1) and charge distribution support this postulation.

While the conjugation of the double anions of the butenediide dianions is discouraged, the anion conjugation is restored as the olefin unit is extended, i.e., the conjugation energy of the hexadienediide dianion **5** is increased to 102 kJ mol^{-1} (estimated by a single constraint (**5A**, Fig. 1) on one of the terminal C–C bonds), the value being comparable to that of the TMM dianion. *This coincidence implies that the merit of the Y-shaped configuration of the TMM dianion is extension of delocalization: the TMM dianion can be regarded as a hexadienediide dianion fan-folded into the Y-shaped structure* (Scheme 1).[31] Finally, the conjugation energy of the

Table 1. Energy Changes (in kJ mol^{-1}) Arising from Single and Double Constraints of π-Conjugation of the Butenediide Dianions and TMM Dianions[a]

	TMM dianion **1**		*E*-Butenediide dianion **3**		*Z*-Butenediide dianion **4**	
Constraint	Single **1A**	Double **1B**	Single **3A**	Double **3B**	Single **4A**	Double **4B**
ΔE	102	267	21	72	24	85
$\Delta\langle T\rangle$[b]	183	489	59	218	61	233
$\Delta\langle V\rangle$[b]	−81	−222	−37	−146	−37	−149
$\Delta\langle T\rangle_\pi$[c]	173	450	46	179	48	193
$\Delta\langle T\rangle_\sigma$[c]	10	39	13	39	13	41
P_{rs}[d]	0.4088		0.1695		0.1807	

a) The energy change ΔE represents the difference in energy between the non-constrained and singly (or doubly) constrained electronic structures. b) $\Delta E=\Delta\langle T\rangle+\Delta\langle V\rangle$. c) $\Delta\langle T\rangle=\Delta\langle T\rangle_\pi+\Delta\langle T\rangle_\sigma$. d) π-Bond order of the bond, subjected to constraint.

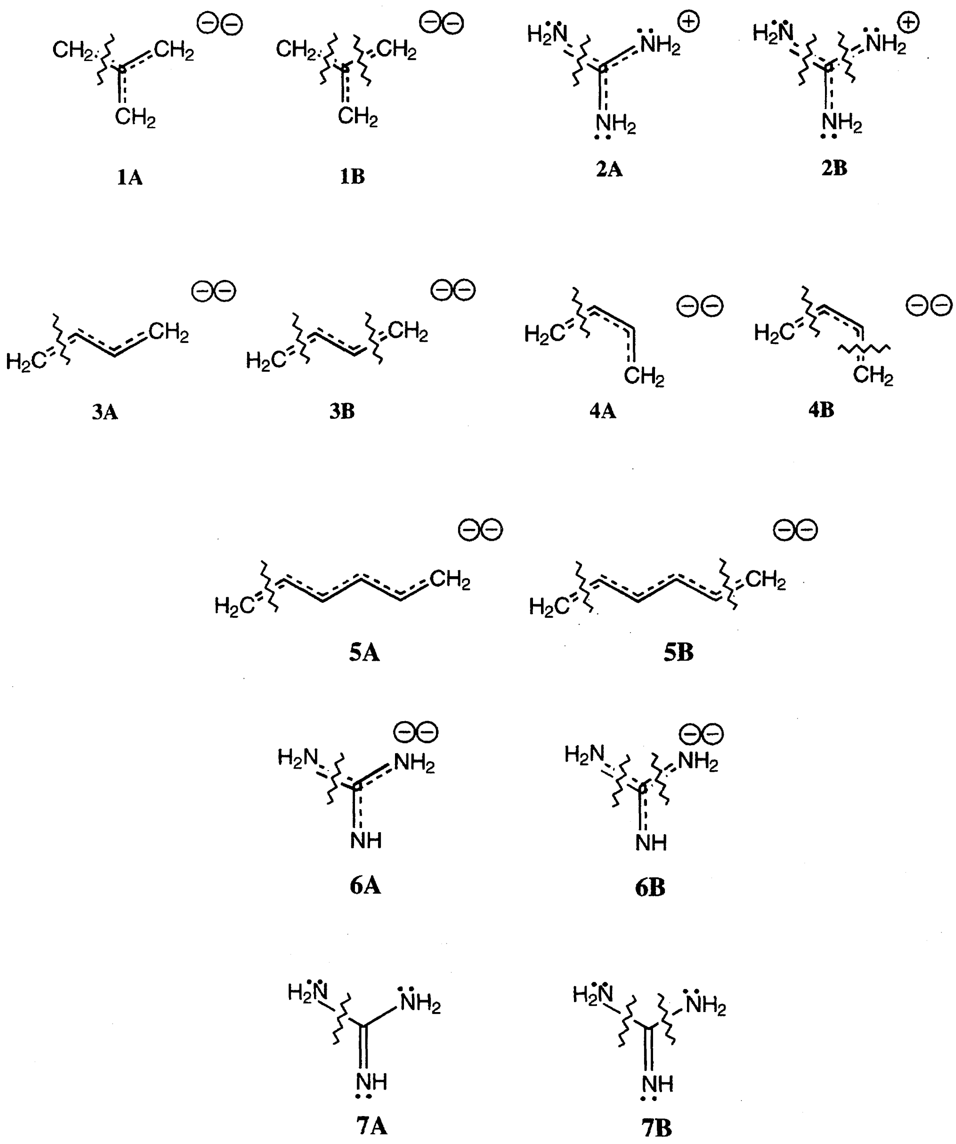


Fig. 1. Constrained conjugations.

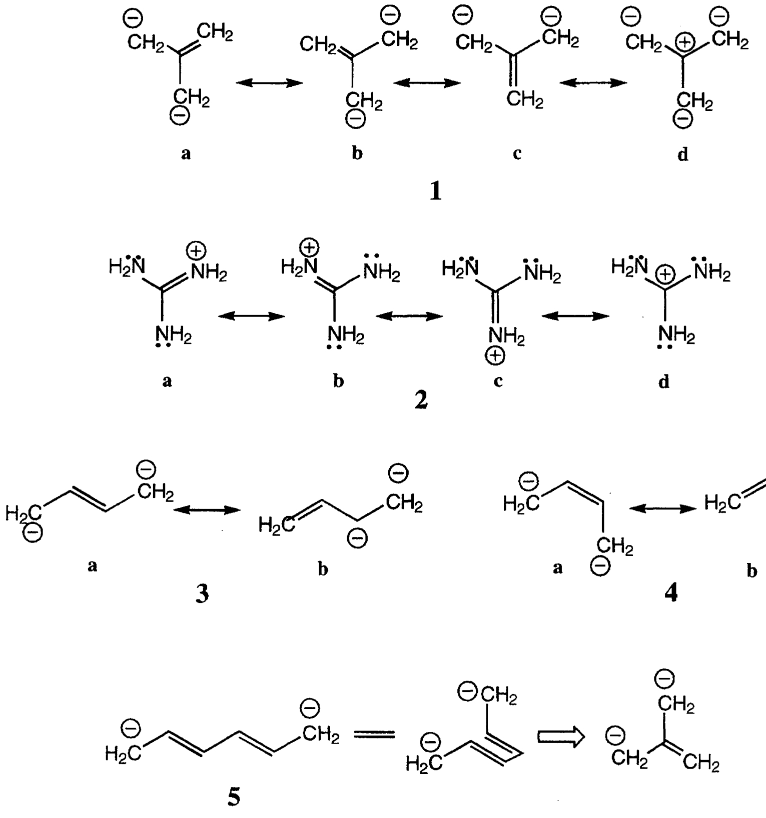
TMM dianion is very much smaller than that of the "typical" aromatic compound, benzene (222 kJ mol^{-1}),[25] suggesting that the Y-conjugative stabilization is not as effective as aromaticity, judging from the magnitude of the value.

Guanidinium Cation. Since the corresponding linear reference species of the guanidinium cation is not conceivable, the conjugative stabilization of the guanidinium ion has been estimated in terms of a rotational barrier[4] and isodesmic reactions.[19] The constrained HF method can provide a direct measurement of the conjugation energy of the guanidinium ion. A single constraint (**2A**) raised the energy by 109 kJ mol^{-1}, and the double constraint (**2B**) gave 277 kJ mol^{-1} (Fig. 1 and Table 3). The magnitude of the first change is comparable to that of the TMM dianion, in spite of the different charges and electronegativities. The guanidine dianion **6**, a hybrid ion of the TMM dianion and the guanidinium cation, can probe these effects on Y-conjugation. As shown in Table 3, the conjugation energies of the guanidine dianion **6** are comparable to those of the TMM dianion and the guanidinium cation, i.e., 118 and 302 kJ mol^{-1} for a single (**6A**) and double (**6B**) constraints, respectively. *These results indicate an intrinsic conjugation effect of the Y-shaped configuration, independent of the total charge and*

Table 2. Energy Changes (in kJ mol^{-1}) Arising from Single and Double Constraints of π-Conjugation of Reference Conjugating Compounds[a)]

	E,*E*-Hexadienediide dianion **5**		Benzene[e)]
Constraint	Single **5A**	Double **5B**	Single
ΔE	102	246	222
$\Delta\langle T\rangle$[b)]	193	494	432
$\Delta\langle V\rangle$[b)]	−91	−248	−210
$\Delta\langle T\rangle_\pi$[c)]	165	418	440
$\Delta\langle T\rangle_\sigma$[c)]	28	76	−8
P_{rs}[d)]	0.3912		0.5045

a, b, c, d) See the captions in Table 1. e) Ref. 25.



Scheme 1.

Scheme 2.

electronegativity (Scheme 2). On the other hand, neutral guanidine **7**, the deprotonated form of the guanidinium ion **2**, also has a Y-shaped geometry, but the delocalization is not encouraged, judging from the conjugation energy relative to the N–C single bonds (a single constraint (**7A**): 29 kJ mol^{-1}; double constraints (**7B**): 60 kJ mol^{-1}).

Energy Component Analysis. The conjugation energy (ΔE) can be analyzed into kinetic ($\Delta\langle T\rangle$) and potential ($\Delta\langle V\rangle$) energy terms, both of which can be further assigned to π and σ components.[23] Here we showed the analysis of the kinetic term into π ($\Delta\langle T\rangle_\pi$) and σ ($\Delta\langle T\rangle_\sigma$) components (Tables 1, 2, and 3). In all cases (**1**–**7**), the suppression of anion (or lone pair) conjugation increases the kinetic energy ($\Delta T>0$), in particular the π component, while the potential energy is decreased (stabilizing, $\Delta V<0$). These changes are the outcome of the localization of electrons closer to one nucleus upon cancellation of conjugation. Therefore, conjugation involves a relaxation of the kinetic-energy pressure of π-electrons.[28,32,33]

Conclusion. We have applied the constrained HF method to the estimation of conjugation of Y-shaped

Table 3. Energy Changes (in kJ mol^{-1}) Arising from Single and Double Constraints of π-Conjugation of the Gunaidinium Cation and Guanidine[a)]

	Guanidinium cation **2**		Guanidine dianion **6**		Guanidine **7**	
Constraint	Single **2A**	Double **2B**	Single **6A**	Double **6B**	Single **7A**	Double **7B**
ΔE	109	277	118	301	29	60
$\Delta\langle T\rangle^{b)}$	251	676	287	800	49	109
$\Delta\langle V\rangle^{b)}$	−142	−399	−169	−498	−20	−49
$\Delta\langle T\rangle_\pi{}^{c)}$	272	744	258	711	115	247
$\Delta\langle T\rangle_\sigma{}^{c)}$	−21	−392	29	88	−66	−138
$P_{rs}{}^{d)}$	0.4089		0.4277		0.1905	

a, b, c, d) See the captions in Table 1.

molecules. This method does not include the effects of the geometrical change, and gives a direct measurement of π-conjugation energy even in the absence of a linear reference. On the basis of the conjugation energies, we can conclude that conjugation of ions in Y-shaped configurations is definitely encouraged, albeit less than that of a neutral cyclic aromatic compound (benzene). This is consistent with the previous conclusions obtained with the different energetic criteria.[4,10,12,14,16—18]

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