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Preference of [6e/4p], [6e/5p], and [6e/6p] Conjugations in Determining Relative Stabilities of Fused Five-Membered Heteroaromatic Isomers

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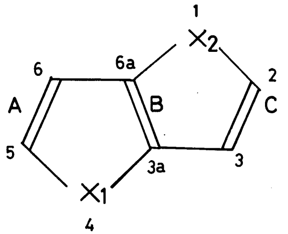
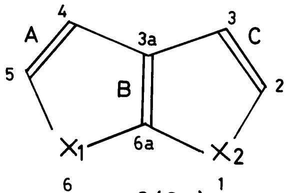
Ab initio molecular orbital calculations showed that fused five-membered heteroaromatics **1** (X=O, NH, S) could be slightly or almost equally stable relative to their isomers **2**. The results suggest that the [6e/6p] triene conjugation is only a little in preference to (or in the balance with) the counteracting [6e/4p] and [6e/5p] conjugations. Kinetically, the isomers **2** were predicted from the qualitative orbital theory and the calculated HOMO energies to be more stable.

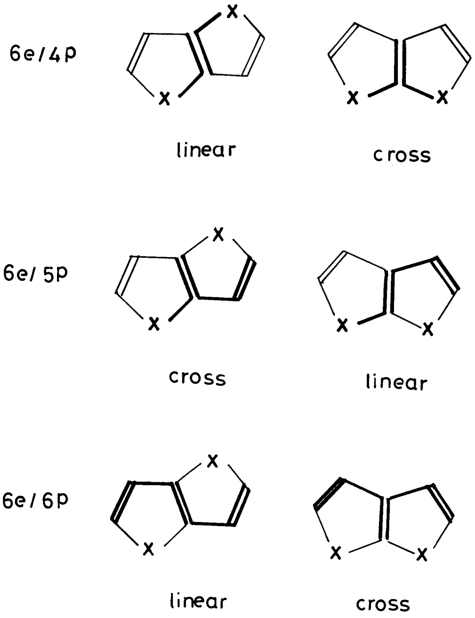
Relationship between relative thermodynamic stabilities of cross vs. linear conjugations and numbers of electrons was previously disclosed in terms of orbital phase continuity-discontinuity properties (Table 1).[1] The cross conjugation is more stable for the system of six electrons in four p-orbitals (hereafter denoted by [6e/4p]). This has been supported by the observed stability of the trimethylenemethane dianion relative to the butadiene dianion.[2] The particular stability of the cross [6e/4p] conjugations has been known as the Y-delocalization.[3] For [6e/6p], the linear conjugation is, conversely, more stable in agreement with the well-known stability of the linear vs. cross conjugated hexatriene. For [6e/5p], the linear conjugation is readily predicted to be more stable. However, we cannot predict thermodynamic preference of cross [6e/4p], linear [6e/5p], and linear [6e/6p] in terms of the orbital phase continuity-discontinuity property.



1 (C_{2h})



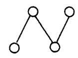
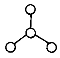
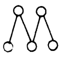
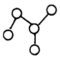
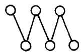
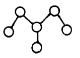
2 (C_{2v})



Scheme 1.

The fused five-membered heteroaromatic molecules and their isomers (**1** and **2**)[4–10] contain [6e/4p], [6e/5p], and [6e/6p] (Scheme 1). The relative stabilities of the isomers is expected to shed light on the thermodynamic preference of these conjugations. The heteroaromatics are composed of three C=C bonds and two heteroatoms (X). The interactions between the neighboring components are supposed to be the most important in determining the stabilities. However, these interactions do not distinguish the isomers from each other. There are no differences between **1** and **2** in the number (two) of the pairs of the neighboring C=C bonds and in the number (four) of pairs of the

Table 1. Relative Stabilities Predicted from Orbital Phase Property[a]

	4p		5p		6p	
						
2e	Unstable	Stable	—	—	—	—
4e	Stable	Unstable	Stable	Unstable	—	—
6e	Unstable	Stable	Stable	Unstable	Stable	Unstable

a) Ref. 1.

neighboring C=C bond and X. The neighboring pair interaction cannot be considered to be a primary factor. It is the three-component interactions that make differences. The X–(C=C)–X system is [6e/4p]. This is linear in **1** and cross in **2**. If [6e/4p] is dominant, **2** should be more stable. The (C=C)–(C=C)–X system is [6e/5p], cross in **1** and linear in **2**. This prefers **2**. The (C=C)–(C=C)–(C=C) system is [6e/6p], which prefers **1** (linear) to **2** (cross).

We theoretically investigated the preference of [6e/4p], [6e/5p], and [6e/6p] in determining the relative thermodynamic stabilities of **1** and **2**. The kinetic stabilities were studied as well.

Results and Discussion

Thermodynamic Stabilities. Molecular geometries of **1** and **2** (X=O, NH, S) were optimized by ab initio molecular orbital calculations with the 3-21G and STO-3G basis sets and the single point calculations (6-31G*//3-21G) were carried out. The heteroaromatics, **1** are only a little more stable than **2** for X=NH, S (Table 2). The results are in agreement with the ordering of the resonance energies (X=S) by Dewar and Trinajstic[11] and by Hess and Schaad,[12] and with the relative STO-3G//MNDO energies (X=NH, S) by Verbist et al.,[13] but not with the lack of the topological resonance energy difference (X=NH, S) by Milun and Trinajstic.[14] For X=O, the thermodynamic preference calculated with the STO-3G and 3-21G basis sets is much smaller. The single point calculation (6-31G*//3-21G) show the reverse ordering of the stabilities. These results suggested that the stabilities are almost equal. This is in agreement with the topological resonance energy.[14]

The slight thermodynamic stabilities of **1** relative to **2** for X=NH and S suggest a little preference of [6e/6p] over [6e/5p] and [6e/4p], since only [6e/6p] prefers **1** as described above. The almost equal stabilities calculated for X=O suggest that the counteracting effects of [6e/5p] and [6e/4p] may be comparable with those of [6e/6p].

Electronic Structures. The electronic structures were scrutinized. The electronic states of **1** and **2** can be described as a linear combination of electron configurations:

$$\psi = C_G\Phi_G + C_T\Phi_T + C_E\Phi_E$$

In the ground configuration, Φ_G, a pair of electrons occupy the bonding orbitals of the C=C bond and the nonbonding orbitals on X. Electrons are neither shifted between any pair of bonds (lone pairs), nor promoted in any bonds. In the electron-transferred configurations, Φ_T, one electron is shifted from a bonding orbital (n-orbital) of a C=C bond (a lone pair) to an antibonding orbital of a bond. In the locally-excited configurations, Φ_E, one electron is promoted from a bonding orbital to an antibonding orbital in a bond. The configuration analysis[15] is the method of calculating the coefficients, C_G, C_T, and C_E, of these configurations. The method of the configuration analysis, originally developed for two-molecule interactions, has been improved for many-system interaction,[16] and applied in a successful manner.[17,18] The extent of electron delocalization and polarization is estimated by the coefficient of the configurations. The coefficient ratios, C_T/C_G and C_E/C_G, has been shown[18] to be good measures rather than C_T and C_E in order to compare the delocalization and polarization at the corresponding parts in different molecules, respectively.

The relative stability of the cross vs. linear [6e/4p] is determined by the C=C bond (B) polarization (Fig. 1). This involves cyclic $\overline{x_1\text{–b–}x_2\text{–b}^*}$ orbital interaction.[1] The orbital phase is continuous in the cross conjugation and discontinuous in the linear conjugation. The contribution of [6e/4p] is here estimated by the bond B polarization (b→b*). The calculated configuration coefficient ratio $C_{E(b\to b^*)}/C_G$ is greater in **2** (Table 3). This is in agreement with the prediction.

The relative stability of the cross and linear [6e/5p] is determined by the delocalization from X_1 to the remote C=C bond (C) (Fig. 2). The cyclic $\overline{x_1\text{–b–c}^*\text{–b}^*}$

Table 2. Total[a] and Relative (ΔE)[b] Energies of **1** and **2**

		1	**2**	ΔE
X=O	STO-3G//STO-3G	−374.39493	−374.39412	−0.51
	3-21G//3-21G	−377.06574	−377.06356	−1.37
	6-31G*//3-21G	−379.17854	−379.18014	1.00
X=NH	STO-3G//STO-3G	−335.34924	−335.34432	−3.09
	3-21G//3-21G	−337.66477	−337.65598	−5.52
	6-31G*//3-21G	−339.55114	−339.54555	−3.51
X=S	STO-3G//STO-3G	−1013.09978	−1013.09811	−1.05
	3-21G//3-21G	−1019.33641	−1019.33114	−3.31
	6-31G*//3-21G	−1024.52684	−1024.52422	−1.64

a) Atomic unit. b) kcal mol^{-1}.

Table 3. Electronic Structure[a] of **1** and **2**

	Electron delocalization								Polarization	
	$X_1 \rightarrow A$		$X_1 \rightarrow B$		$A \rightarrow C$ (6e/6p)		$X_1 \rightarrow C$ (6e/5p)		B (6e/4p)	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**
X=O	0.333	0.305	0.319	0.344	0.059	0.023	0.014	0.064	0.0	0.066
X=NH	0.392	0.355	0.347	0.368	0.064	0.026	0.030	0.071	0.0	0.080
X=S	0.259	0.246	0.251	0.262	0.058	0.010	0.006	0.057	0.0	0.031

a) The coefficient ratio of the electron configuration (See the text). The configuration analysis was carried out using optimized structure at 3-21G levels.

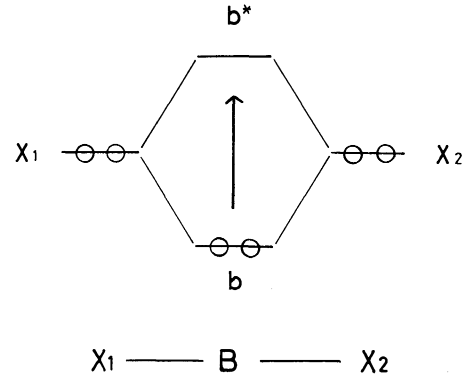


Fig. 1. Polarization of bond B in 6e/4p.

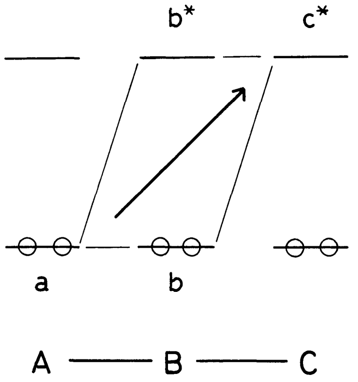


Fig. 3. Delocalization from A to C in 6e/6p.

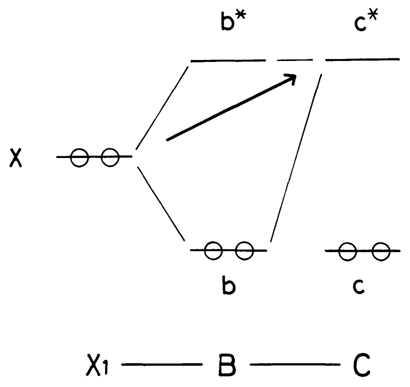


Fig. 2. Delocalization from X_1 to C in 6e/5p.

interaction is involved. The orbital phase is continuous in the linear conjugation (**2**) and discontinuous in the cross conjugation (**1**). The coefficient ratio $C_{T(x1-c^*)}/C_G$ is greater in **2**, in agreement with the prediction.

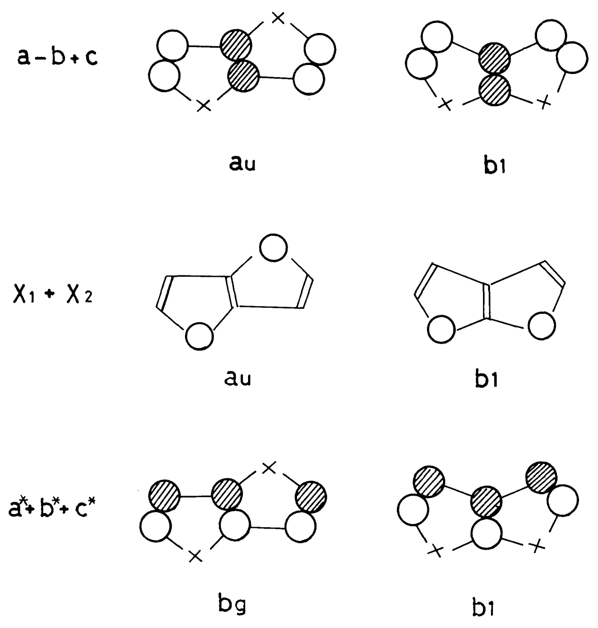
The relative stability of the cross and linear [6e/6p] is determined by the electron delocalization between the terminal C=C bonds (A and C) (Fig. 3). The delocalization from A to C involves cyclic $\overline{a-b-c^*-b^*}$ interaction. The orbital phase is continuous in the linear conjugation (**1**) and discontinuous in the cross conjugation (**2**). The coefficient ratio $C_{T(a-c^*)}/C_G$ is greater in **1**, in agreement with the prediction.

The delocalization between the terminal bonds of the linear [6e/6p] hexatriene in **1** increases in the order of X=S(0.058)≤O(0.059)<NH(0.064). The thermodynamic preference of **1** to **2** increases in the order of X=S<NH as the energy differences between the isomers show (Table 2). The identical orderings supports a little preference of [6e/6p] for X=NH and S.

The almost equal stabilities for X=O can be interpreted in terms of the counteracting effects of [6e/4p] and [6e/5p]. The delocalization in the linear [6e/5p] in **2** is effective for X=O (0.064) relative to S (0.057). The polarization in the cross [6e/4p] in **2** is also more effective for X=O(0.066) than for X=S (0.031). These conjugations have the effects opposite to those of [6e/6p], possibly leading to almost the same stabilities of the isomers. The increase in the counteracting effects for X=O results from the effective delocalization between the adjacent X and C=C bonds, indispensable for [6e/4p] and [6e/5p].[19] The delocalization effectively occurs for X=O relative to S, as is seen in the $X_1 \rightarrow A$ and $X_1 \rightarrow B$ delocalization (Table 3).

Kinetic Stabilities. The stabilities of molecules encountered in preparation are of kinetic as well as thermodynamic origins. The kinetic stability of cyclic conjugated molecules is not necessarily parallel with the thermodynamic stability.[20] A simple measure of kinetic stability is the frontier orbital energy. The heteroaromatics of the present interest are π-excessive molecules, and may work as electron donors in most of chemical reactions. The HOMO energy is a good measure of the kinetic stability.

We can predict the relative HOMO energies of **1** and **2** on the basis of the qualitative orbital theory (Scheme



Scheme 2.

2). In order to use the symmetry of the molecule for simplifying argument, **1** and **2** are supposed to be composed of the lone pair group and the triene group. The HOMO of the triene group is an out-of-phase combination of the bonding orbitals of each C=C bond, a_u in **1** (C_{2h}) and b_1 in **2** (C_{2v}). The HOMO of the lone pair group is an in-phase or out-of-phase combination of the n-orbitals almost degenerate due to weak interaction at a long distance. The in-phase combined n-orbitals is allowed by symmetry (a_u in **1** and b_1 in **2**) to interact with the triene HOMO. The resulting high-lying orbital is the primary component of the HOMO of the whole molecule. At this level, the HOMO energy is not considered to be different between **1** and **2**. The secondary component of the HOMO is the LUMO of the triene group, which is mixed through the interaction with the n-orbitals. The triene LUMO is an in-phase combination of the antibonding orbital of each C=C bond, b_g in **1** and b_1 in **2**. In **1** the triene LUMO (b_g) cannot be mixed by the symmetry into the primary HOMO component (a_u).

Table 4. HOMO Energies[a)] and Orbital Amplitude[b)] of **1** and **2**

	1		**2**	
X=O	−0.3060 (STO-3G//STO-3G)		−0.3128 (STO-3G//STO-3G)	
	−0.2393 (3-21G//3-21G)		−0.2474 (3-21G//3-21G)	
	−0.2911 (6-31G*//3-21G)		−0.2974 (6-31G*//3-21G)	
	O(1)	0.006	O(1)	0.143
	C(2)	−0.470	C(2)	0.443
	C(3)	−0.254	C(3)	0.155
	C(3a)	0.449	C(3a)	−0.458
	O(4)	0.006	C(4)	0.155
	C(5)	−0.470	C(5)	0.433
	C(6)	−0.254	C(6)	0.143
	C(6a)	0.449	C(6a)	−0.536
X=NH	−0.2580 (STO-3G//STO-3G)		−0.2627 (STO-3G//STO-3G)	
	−0.1986 (3-21G//3-21G)		−0.2040 (3-21G//3-21G)	
	−0.2510 (6-31G*//3-21G)		−0.2558 (6-31G*//3-21G)	
	N(1)	0.029	N(1)	−0.163
	C(2)	−0.474	C(2)	−0.444
	C(3)	−0.250	C(3)	−0.111
	C(3a)	0.444	C(3a)	0.490
	N(4)	0.029	C(4)	−0.111
	C(5)	−0.474	C(5)	−0.444
	C(6)	−0.250	N(6)	−0.163
	C(6a)	0.444	C(6a)	0.514
X=S	−0.3185 (STO-3G//STO-3G)		−0.3230 (STO-3G//STO-3G)	
	−0.2322 (3-21G//3-21G)		−0.2334 (3-21G//3-21G)	
	−0.3077 (6-31G*//3-21G)		−0.3108 (6-31G*//3-21G)	
	S(1)	0.293	S(1)	−0.275
	C(2)	−0.420	C(2)	−0.399
	C(3)	−0.357	C(3)	−0.099
	C(3a)	0.311	C(3a)	0.497
	S(4)	0.293	C(4)	−0.099
	C(5)	−0.420	C(5)	−0.399
	C(6)	−0.357	S(6)	−0.275
	C(6a)	0.311	C(6a)	0.483

a) Atomic unit. b) Calculated at STO-3G level.

The HOMO is not stabilized. In **2** these orbitals are allowed by symmetry (b_1) to interact with each other, leading the stabilization of the HOMO. As a result, the HOMO energy is predicted to be lower in **2**, or **2** is predicted to be kinetically more stable.

The ab initio molecular orbital calculations with the STO-3G, 3-21G and 6-31G*//3-21G basis sets confirmed the prediction (Table 4). This is in agreement with the relative HOMO energies (X=NH, S) calculated by the MNDO and STO-3G//MNDO calculations[13] and with the observed ionization potentials for X=S[6]. These results showed that **2** is kinetically more stable than **1**.

The present calculations also confirmed the prediction of the HOMO symmetry (a_u for **1** and b_1 for **2**)[7,13] reported so far except the HMO result for **2** (X=NH).[7] The orbital amplitude is in agreement with the methyl substituent effect on the vertical ionization energies and the selectivity of electrophilic substitution reactions of **2** (X=NH).[21]

Conclusion

We have investigated the preference of the [6e/4p], [6e/5p], and [6e/6p] conjugations in determining thermodynamic stability of the fused five-membered heteroaromatic isomers, **1** and **2** (X=O, NH, S). Ab initio molecular orbital calculations showed that the heteroaromatics **1** (X=O, NH, S) containing the linear [6e/6p] conjugation is slightly or almost equally stable relative to the isomer **2** containing the cross [6e/4p] and linear [6e/5p]. The result suggests that the linear [6e/6p] is a little in preference to (or in the balance with) [6e/5p] and/or [6e/4p]. These interpretations were substantiated by the configuration analysis of the electronic structures.

The heteroaromatics **2** were predicted in terms of the HOMO energy to be kinetically more stable than the isomers **1**. The LUMO of the triene group can be mixed into the primary components of the HOMO of the whole molecule, i.e., the HOMO of the triene group and the n-orbitals, due to the symmetry (b_1) matching in **2** (C_{2v}), while not due to the symmetry mismatching (a_u and b_g) in **1** (C_{2h}).

Ab initio molecular orbital calculations with Gaussian 80 and MONSTERGAUSS programs were carried out on a HITAC M-680H computer at the Institute for Molecular Science and on a FACOM M-782 computer at Nagoya University Computer Center, respectively. We are grateful to Professor Kimihiko Hirao for permitting us to use MONSTERGAUSS program. The configuration analysis was carried out on a FACOM M-360 computer at Gifu University Computing Center. This work was supported by a Grant-in-Aid for Co-operative Research from the Ministry of Education, Science, and Culture.

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