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Orbital phase control of conformations of alkyne derivatives

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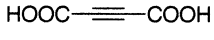
Abstract—Stable conformers of the alkynes bis-substituted by donor (NH_2) and/or acceptor (CHO) groups were predicted by the orbital phase theory and confirmed by the ab initio and density functional calculations. The most stable conformers are planar in the mono-, di-, and triacetylenes substituted by a donor on terminal carbon atom and an acceptor on the other one. The stable conformers of those with donors or acceptors on both terminal carbon atoms are orthogonal. In the most stable conformers of the equatorial isomers of the hypervalent derivatives ($RC{\equiv}CSiF_4^-$: R=NH_2; CHO), the donor (n_N) orbital and $\sigma^*_{SiF_{eq}}$ with same π_{CC} bond orbitals, or the acceptor (π^*_{CO}) orbital and $\sigma^*_{SiF_{eq}}$ interact with different π_{CC} bond orbitals.

1. Introduction

Cyclic orbital interactions were previously shown to be involved even in acyclic conjugations.[1] The stabilities of acyclic conjugated systems are controlled by the continuity–discontinuity properties of the orbital phase. The orbital phase theory has been successfully applied to the relative stabilities of the cross and linear π conjugated isomers with both closed-[2] and open-[3] shell electronic structures, to those of σ conjugated isomers,[4] to the regioselectivities of organic reactions,[5] to the abnormally acute coordinate angle of metal complexes,[6] and to the conformational stabilities of α- and β-substituted enamines and vinyl ethers.[7]

Conformations of alkyne derivatives have rarely been documented so far. Acetylenedicarboxylic acid (**1**) has non-planar conformer. The dihedral angle between the carboxy groups is 57.8° by X-ray analysis.[8] The most stable conformer of 3-(4-iodomethyl-2-oxo-1-azetidinyl)-propynoic acid *tert*-butyl ester (**2**) is planar. The dihedral angle between C=O and NC=O groups is 7.8° by X-ray analysis.[9] In this paper, the orbital phase theory was applied to predict the stable conformers of alkyne derivatives **3**–**19**. Among them are included mono-, di-, and triacetylenes substituted by the CH_2^- and NH_2 groups as a donor, by CH_2^+, CH, and CHO groups as an acceptor and by SiF_4^- as a hypervalent group.



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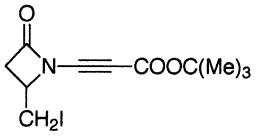

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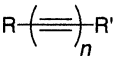

3: n = 1, R = NH_2, R' = CHO
4: n = 1, R = R' = CHO
5: n = 1, R = R' = NH_2
6: n = 2, R = NH_2, R' = CHO
7: n = 2, R = R' = CHO
8: n = 2, R = R' = NH_2
9: n = 3, R = NH_2, R' = CHO
10: n = 3, R = R' = CHO
11: n = 3, R = R' = NH_2
12: n = 1, R = CH_2^+, R' = NH_2
13: n = 1, R = CH_2^+, R' = CHO
14: n = 1, R = CH_2^-, R' = NH_2
15: n = 1, R = CH_2^-, R' = CHO
16: n = 1, R = CH, R' = NH_2
17: n = 1, R = CH, R' = CHO
18: n = 1, R = SiF_4^-, R' = NH_2
19: n = 1, R = SiF_4^-, R' = CHO

2. Results and discussion

2.1. Mono-, di-, triacetylenes

There can be planar and orthogonal conformations of alkyne

Keywords: orbital phase; comformation; bis-substituted alkene; hypervalent molecule.

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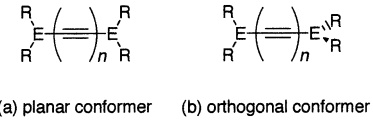


Figure 1. Planar (a) and orthogonal (b) conformers of alkynes.

derivatives (Fig. 1). When acetylene is substituted by π electron- accepting groups (X), e.g. CH_2^+, CH, and CHO groups, and π electron-donating (Y), e.g. NH_2 and CH_2^- groups (XC≡CY), π electron-accepting orbital (π_X^*) including the vacant p-orbital on the C atom in CH_2^+ and CH and the antibonding orbital of π_{CO} bond, and the lone pair n_Y of N atom in NH_2 and C atom in CH_2^- interact with the same π_{CC} bond orbitals of acetylene in the planar conformer. There are the π_X^*—π_{CC}, π_{CC}—n_Y, n_Y—π_{CC}^*, and π_{CC}^*—π_X^* orbital interactions, i.e. cyclic —π_X^*—π_{CC}—n_Y—π_{CC}^*— orbital interactions [Fig. 2(a)]. In the orthogonal conformer, the π_X^* and n_Y orbitals interact with the different π_{CC} bond orbitals of acetylene. There are acyclic π_{CC}—π_X^*—π_{CC}^* and π_{CC}'—n_Y—$\pi_{CC}^{*\prime}$ interactions. When both terminals of acetylene are substituted by X or Y (XC≡CX or YC≡CY), the π_X^*s and n_Ys interact with the same π_{CC} bond orbitals in the planar conformer. There are two π_{CC}—π_X^* and two π_X^*—π_{CC}^* orbital interactions, i.e. cyclic —π_{X1}^*—π_{CC}—π_{X2}^*—π_{CC}^*— orbital interactions in XC≡CX, and two n_Y—π_{CC} and two n_Y—π_{CC}^* orbital interactions, i.e. cyclic —n_{Y1}—π_{CC}—n_{Y2}—π_{CC}^*— orbital interaction in YC≡CY [Fig. 2(b) and (c), respectively]. In the orthogonal conformer, π_X^* and n_Y orbitals interact with the different π_{CC} bond orbitals. There are no cyclic orbital interactions.

Cyclic orbital interactions are required for effective occurrence to meet the following conditions:[1] (i) the bonding or nonbonding (occupied) orbitals are out of phase; (ii) the antibonding (unoccupied) orbitals are in phase; and (iii) the bonding (nonbonding) and antibonding orbitals are in phase. When the conditions are satisfied simultaneously, the orbital phase is continuous. The cyclic interaction significantly contributes to stabilization. Otherwise, the phase is discontinuous, and the cyclic orbital interaction does not effectively contribute to stabilization. If the orbital phase is continuous in the planar conformers, the planar conformers are more stable than the orthogonal conformers. If the orbital phase in the planar conformers is discontinuous, the planar conformers are less stable than the orthogonal conformers.

Table 1. The relative energies ΔE[a] (in kcal/mol) of the conformers of bis-substituted acetylenes (n=1), diacetylenes (n=2), and triacetylenes (n=3)

Substituents	ΔE		
	n=1	n=2	n=3
NH_2, CHO	−3.89 (−5.84)	−1.50 (−2.98)	−0.69 (−1.77)
CHO, CHO	0.67 (0.95)	0.38 (0.78)	0.19 (0.54)
NH_2, NH_2	3.10 (5.18)	2.16 (3.27)	1.03 (2.08)

[a] $\Delta E = E_{planar} - E_{orthogonal}$. The values of HF/6-31+G* calculations are shown. The values of B3LYP/6-31+G* calculations are shown in parentheses.

The stable conformer of XC≡CY was predicted from the orbital phase theory to be planar. The phase of the —π_X^*—π_{CC}—n_Y—π_{CC}^*— orbitals in the planar conformer is continuous [Fig. 2(a)]: the accepting π_X^* and donating π_{CC} orbitals are in phase; the donating π_{CC} and n_Y orbitals are out of phase; the donating n_Y and accepting π_{CC}^* orbitals are in phase; the accepting π_{CC}^* and π_X^* orbitals are in phase. The stable conformers of XC≡CX and YC≡CY were predicted to be orthogonal. The phases of the —π_X^*—π_{CC}—π_X^*—π_{CC}^*— orbitals and —n_Y—π_{CC}—n_Y—π_{CC}^*— orbitals in the planar conformers are discontinuous [Fig. 2(b) and (c)]. In XC≡CX, the π_{CC} and π_X^* orbitals and the π_X^* and π_{CC}^* orbitals are required to be in phase. However, all the requirements are not simultaneously satisfied. In YC≡CY, the π_{CC} and n_Y orbitals and the n_Y and π_{CC}^* orbitals are required to be out of phase and in phase. However, this is not the case.

The molecules **3**–**19** were calculated at the HF/6-31+G* and B3LYP/6-31+G* level to examine the predictions.[10] In **3**, the planar conformer is more stable by 3.9–5.8 kcal/mol

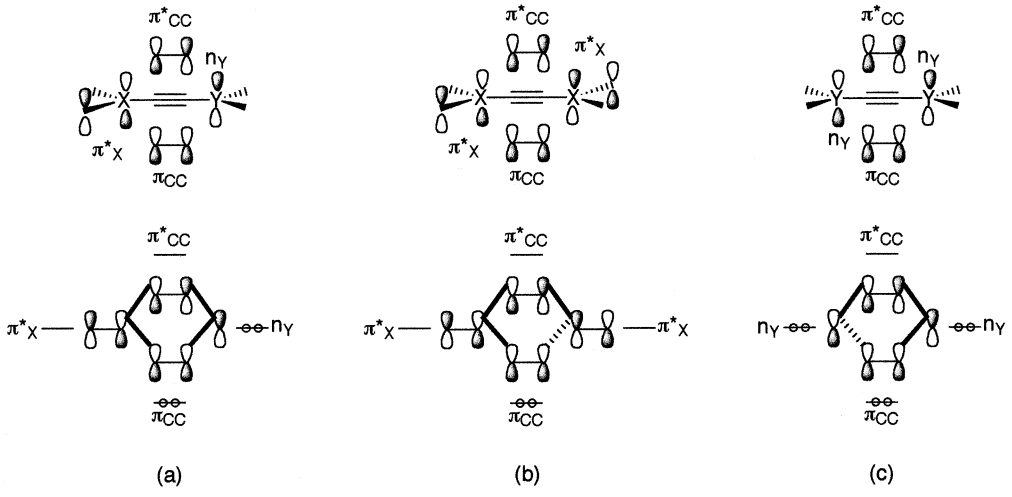


Figure 2. Cyclic orbital interactions and orbital phase properties in the planar conformers of the bis-substituted acetylenes.

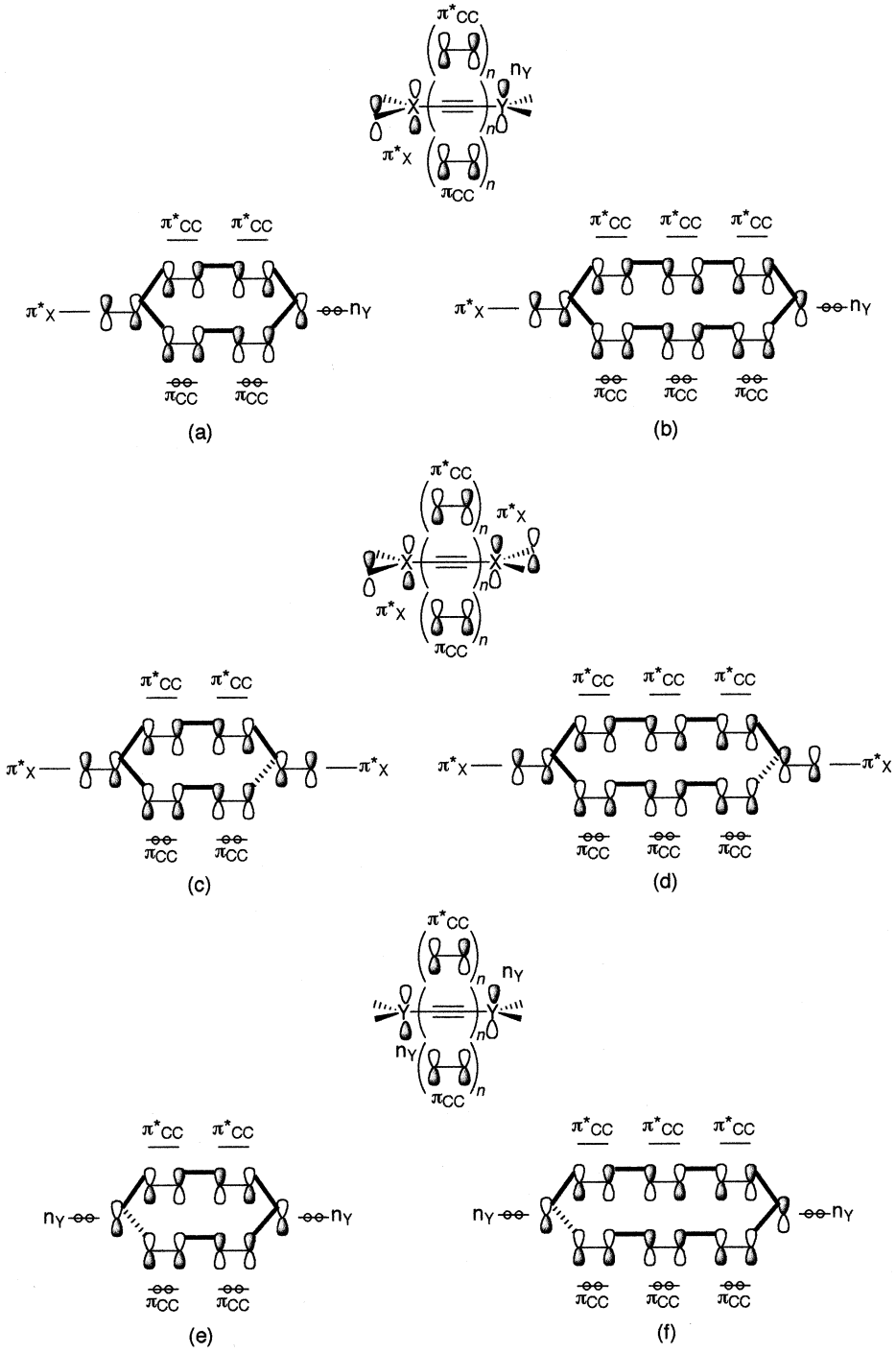


Figure 3. Cyclic orbital interactions and orbital phase properties in the planar conformers of the bis-substituted di- [(a), (c), and (e)] and triacetylenes [(b), (d), and (f)].

than the orthogonal conformer (Table 1). In **4**, the orthogonal conformer is more stable by 0.7–1.0 kcal/mol than the planar conformer. In **5**, the orthogonal conformer is more stable by 3.1–5.2 kcal/mol than the planar conformer. These calculational results are in agreement with the orbital phase predictions. The less stable conformers are the transition structures for the rotation. The orbital phase predictions are also supported by the experimental observations. The stable conformer of acetylenedicarboxylic acid (**1**)[8] is orthogonal while 3-(4-iodomethyl-2-oxo-1-azetidinyl)-propynoic acid *tert*-butyl ester (**2**) has a planar conformation.[9]

The stable conformers of the di- and triacetylene derivatives (**6**–**11**) are similarly predicted to be the same as acetylene derivatives: planar in **6** and **9** and orthogonal in **7**, **8**, **10**, and **11**. The orbital phases involved in the cyclic interactions in the planar conformers are continuous in **6** and **9**, and discontinuous in **7**, **8**, **10**, and **11** (Fig. 3). The predictions were confirmed by the calculations. In **6** and **9**, the planar

Table 2. The relative energies ΔE[a] (in kcal/mol) of the conformers of the cation, anion, and carbene derivatives

Substituents	ΔE		
	Cation	Anion	Carbene
NH_2	−33.85 (−35.63)	5.95 (7.24)[b]	−21.67 (−28.58)[c]
CHO	3.23 (6.05)	−8.62 (−12.32)	8.56 (14.11)

[a] $\Delta E = E_{planar} - E_{orthogonal}$. The values of HF/6-31+G* calculations are shown. The values of B3LYP/6-31+G* calculations are shown in parentheses.
[b] The orthogonal conformation is transition states. The most stable isomer is allene form.
[c] The planar conformer is transition state. The most stable isomer is formyl ethynyl carbene.

conformer is more stable by 1.5–3.0 and 0.7–1.8 kcal/mol than the orthogonal conformer, respectively (Table 1). In **7**, **8**, **10**, and **11**, the orthogonal conformers are more stable by 0.4–0.8, 2.2–3.3, 0.2–0.5, and 1.0–2.1 kcal/mol than the planar conformers, respectively (Table 1). The relative stabilities decrease of 25–60% with each acetylene unit extension. The orbital phase predictions are in agreement with the experimental observations.[11–14] The observed conformers of *N*-(4-acetylbuta-1,3-diynyl)molpholine (**20**),[11] *N*-(4-acetoxybuta-1,3-diynyl)molpholine (**21**),[11] 6-(methylphenylamino)-3,5-hexadiyn-2-one (**22**),[11] and 5-(diphenylamino)-1-phenylpenta-2,4-diyn-1-one (**23**)[12] are the planar conformers (the dihedral angles ϕCNCO are 2.6, 19.2, 1.1, and 3.0° in **20**, **21**, **22**, and **23** by X-ray analysis, respectively). The most stable conformers of diacetylenedicarboxylic acid dihydrate (**24**)[13] and bis(1-carbazolyl)butadiyne (**25**)[14] are orthogonal conformers (ϕOCCO=57.0° in **24**, ϕCNNC=85.0° in **25** by X-ray analysis).

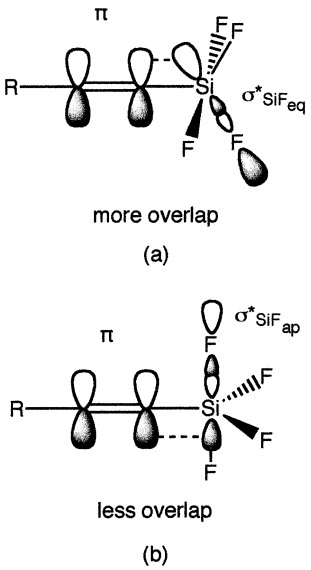
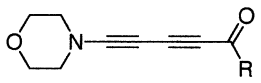
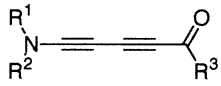


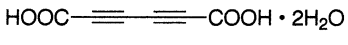
Figure 4. (a) π-$\sigma^*_{SiF_{eq}}$ and (b) π-$\sigma^*_{SiF_{ap}}$ interactions in RC≡ $CSiF_4^-$.



20: R = Me
21: R = OMe



22: R^1 = Me, R^2 = Ph, R^3 = Me
23: R^1 = R^2 = R^3 = Ph



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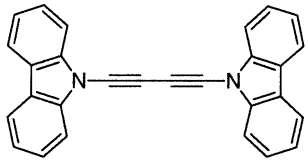

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In the cation, anion, and singlet carbene derivatives (**12**–**17**), the vacant p_C orbital of the CH_2^+ and CH group is π accepting orbital and occupied n_C orbital of the CH_2^- group is π donating orbital. The most stable conformers of amino substituted cation and carbene derivatives (**12**, **16**) and formyl substituted anion derivative (**15**) are predicted to be planar because of the phase continuity of the cyclic $-n_N-\pi_{CC}-p_C-\pi^*_{CC}-$ and $-\pi^*_{CO}-\pi_{CC}-n_C-\pi^*_{CC}-$ $_{CC}-n_C-\pi^*_{CC}-$ orbitals in planar conformers, respectively. The most stable conformers of formyl substituted cation and carbene derivatives (**13**, **17**) and amino substituted anion derivative (**14**) are predicted to be orthogonal because of the phase discontinuity of the cyclic $-\pi^*_{CO}-\pi_{CC}-p_C-\pi^*_{CC}-$ and $-n_N-\pi_{CC}-n_C-\pi^*_{CC}-$ orbitals in planar conformers, respectively.

In **12**, **15**, and **16**, the planar conformer is more stable by 33.9–35.6, 8.6–12.3, and 21.7–28.6 kcal/mol than the orthogonal conformer, respectively (Table 2). In **13**, **14**, and **17**, the orthogonal conformer is more stable by 3.2–6.1, 6.0–7.2, 8.6–14.1 kcal/mol than the planar conformer, respectively (Table 2). These results are in agreement with the predictions. However, both planar and orthogonal conformations of **14** and **16** are transition states. The stable isomer of **14** is 1-aminoallenyl anion ($NH_2C^-=C=CH_2$). The stable isomer of **16** is 1-amino ethynylcarbene ($NH_2C-C\equiv CH$) due to the stabilization by the strong interaction of n_N with the vacant p-orbital of the carbene.

2.2. Hypervalent substituents

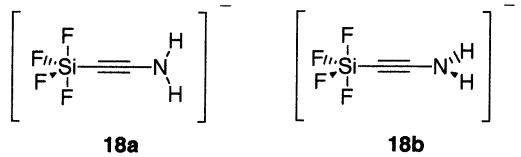
In RC≡$CSiF_4^-$ (**18**: R=NH_2 and **19**: R=CHO), the equatorial isomers are more stable than the apical isomers due to the high apicophilicity of fluorine atom.[15] There are two conformers in the equatorial isomer. The NH or CO bond eclipses with the apical SiF bonds (**18a** and **19a**) or with the equatorial SiF bonds (**18b** and **19b**). An SiF bond is

Table 3. The relative energies ΔE[a] (in kcal/mol) of the conformers of **18** and **19**

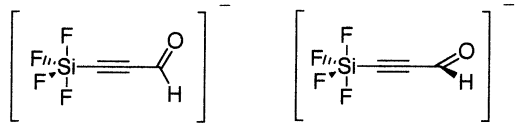
	ΔE
18	2.97 (2.97)
19	−2.15 (−2.39)

[a] $\Delta E=E_{\mathbf{18a}}-E_{\mathbf{18b}}$ and $E_{\mathbf{19a}}-E_{\mathbf{19b}}$. The values of HF/6-31+G* calculations are shown. The values of B3LYP/6-31+G* calculations are shown in parentheses.

electron-withdrawing. The equatorial σ^*_{SiF} orbital interacts with π_{CC} more than the apical σ^*_{SiF} orbital due to the large overlap (Fig. 4). Cyclic orbital interaction involving $\sigma^*_{SiF_{eq}}$ is expected to be more significant. In **18a** and **19a**, the n_N orbital in the amino group or the π^*_{CO} orbital in the formyl group interact with the same π_{CC} bond orbitals as $\sigma^*_{SiF_{eq}}$ but with different π_{CC} bond orbitals in **18b** and **19b**. There is the cyclic interaction of n_N (or π^*_{CO}), π_{CC}, π^*_{CC}, and $\sigma^*_{SiF_{eq}}$ in **18a** and **19a**. In the amino derivative, the cyclic $-n_N-\pi_{CC}-\sigma^*_{SiF_{eq}}-\pi^*_{CC}-$ orbital interaction is favored by the orbital phase continuity **18a**. The isomer **18a** is predicted to be more stable than **18b**. In the formyl isomer **19a** the $-\pi^*_{CO}-\pi_{CC}-\sigma^*_{SiF_{eq}}-\pi^*_{CC}-$ orbital interaction is disfavored by the phase discontinuity. The isomer **19a** is predicted to be less stable than **19b**. In fact, **18a** is more stable by 3.0 kcal/mol than **18a** (Table 3). The isomer **19a** is less stable by 2.2–2.4 kcal/mol than **19b**. The less stable isomers **18b** and **19a** were found to be the transition structures. These results are in agreement with the predictions. The apical isomer is less stable by 4.9–5.0 and 1.3–1.5 kcal/mol than the most stable equatorial isomer in **18** and **19**, respectively.



18a **18b**



19a **19b**

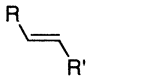
2.3. Comparison with ethylene derivatives

The stable conformers of the ethylene derivatives can also be predicted as the acetylene derivatives. In amino formylethylene (**26**), the planar conformer is more stable than the orthogonal conformer. In diformylethylene (**27**) and diaminoethylene (**28**), the orthogonal conformers are more stable. In **26**, the planar conformer was calculated to be more stable by 9.2–12.7 kcal/mol than the orthogonal conformer (Table 4), in agreement with the prediction. The orthogonal conformer is a transition structure. In **27**, the planar conformer is more stable by 6.9–7.4 kcal/mol than the orthogonal conformer, a transition structure (Table 4). In **28**, the orthogonal conformer is more stable (0.6 kcal/mol) in the HF calculation and is less stable (0.6 kcal/mol) in the B3LYP calculation than the planar conformer (Table 4). Both conformers are local energy minima. The results of **27** and **28** are not in agreement with the predictions.

Table 4. The relative energies ΔE[a] (in kcal/mol) of the conformers of bis-substituted ethylenes

Substituents	ΔE
NH_2, CHO	−9.20 (−12.71)
CHO, CHO	−6.91 (−7.43)
NH_2, NH_2	0.61 (−0.61)

[a] $\Delta E=E_{planar}-E_{orthogonal}$. The values of HF/6-31+G* calculations are shown. The values of B3LYP/6-31+G* calculations are shown in parentheses.



26: R = NH_2, R' = CHO
27: R = R' = CHO
28: R = R' = NH_2

The bond model analysis[16] were employed to understand the disagreement between the predictions and the calculations. In **27** and **28**, the delocalization from the π_{CC} orbital to the π^*_{CO} orbital and from the n_N orbital to the π^*_{CC} orbital (π conjugated one) were less in the planar conformer ($|C_T/C_G|=0.124$; IBE=−0.392 au and $|C_T/C_G|=0.11$; IBE=−0.287 au) than in the orthogonal conformer ($|C_T/C_G|=0.12$; IBE=−0.437 au and $|C_T/C_G|=0.141$; IBE=−0.397 au), respectively. These results supported that the cyclic interactions involving the $\pi_{CC}\rightarrow\pi^*_{CO}$ and the $n_N\rightarrow\pi^*_{CC}$ delocalizations should be disfavored by the orbital phase discontinuity in the planar conformers. However, there are two $\pi_{CC}-\pi^*_{CO}$ and $n_N-\pi^*_{CC}$ interactions in the planar conformers and one $\pi_{CC}-\pi^*_{CO}$ and $n_N-\pi^*_{CC}$ interactions in the orthogonal conformers. The total stabilization by the π delocalization between the neighboring groups is larger in the planar conformers than in the orthogonal conformers. These results showed that the acyclic neighboring orbital interaction is predominant rather than the cyclic orbital interaction.

3. Conclusion

The orbital phase theory was applied to the conformational stabilities of the alkyne bis-substituted by such electron donors, as NH_2 and CH_2^- groups and/or such electron acceptors as COH, CH_2^+, and :CH groups. The most stable conformers were then predicted to be planar in the mono-, di-, triacetylenes substituted by a donor on a terminal carbon and an acceptor on the other and to be orthogonal in those substituted by donors or acceptors on both terminal carbons. The predictions were confirmed by ab initio and density functional calculations and were supported by the experimental observations.

The planar and orthogonal conformations of $NH_2C\equiv C-CH_2^-$ and $NH_2C\equiv C-CH$ are transition structures. The stable

isomers are allenic molecules, $NH_2C^-{=}C{=}CH_2$ and $NH_2C{-}C{\equiv}CH$.

In the hypervalent derivatives ($RC{\equiv}CSiF_4^-$), the equatorial isomers are more stable than the apical isomers due to the apicophilicity of the fluorine atom. In the equatorial isomer, the equatorial σ^*_{SiF} orbital interacts with the π_{CC} orbital more than the apical σ^*_{SiF} because of the large $\pi_{CC}{-}\sigma^*_{SiF_{eq}}$ overlap. When R is a donor, the conformers in which the donor orbital interacts with the same π_{CC} bond orbitals as $\sigma^*_{SiF_{eq}}$, are more stable. When R is an acceptor, the conformers in which the acceptor orbital interacts with the different π_{CC} bond orbitals as $\sigma^*_{SiF_{eq}}$, are more stable.

The stable conformers of the ethylenes with a donor group on a carbon atom and an acceptor groups are planar in agreement of the orbital phase prediction. The stable conformers of the ethylenes substituted by donor or acceptor groups on both carbon atoms are planar. Otherwise, the planar conformers are as stable as the orthogonal conformers. The stabilities are not in agreement with the orbital phase prediction. The disagreements result from the predominance of the acyclic neighboring orbital interaction rather than the cyclic orbital interaction.

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16. We proposed and applied a bond model to analyze the electronic structures of molecules[1–6,17,18] and transition states.[19,20] The single Slater determinant of the Hartree–Fock wave function (Φ) for the electronic structure of the molecule or the transition state is expanded into electron configurations:[3b]

$$\Psi = C_G\Phi_G + \Sigma C_T\Phi_T + \Sigma C_E\Phi_E + \cdots$$

In the ground configuration (Φ_G), a pair of electrons occupies each bonding orbital of the bonds. The interactions between the bond orbitals are accompanied by electron delocalization and polarization. The delocalization is expressed by mixing an electron-transferred configuration (Φ_T), where an electron shifts from the bonding orbital of a bond to the antibonding orbital of another. The polarization is expressed by mixing a locally-excited configuration (Φ_E) where an electron is promoted from the bonding orbital to the antibonding orbital of bond. A set of bond orbitals, i.e. hybrid orbitals and bond polarities give the coefficients of the configurations, C_G, C_T, and C_E. The bonding and antibonding orbitals ϕ_i and ϕ_i^* of the ith bond are expressed by a linear combination of hybrid atomic orbitals ϕ_{ia} and ϕ_{ib} on the bonded atoms a and b:

$$\phi_i = c_{ia}\chi_{ia} + c_{ib}\chi_{ib}$$

$$\phi_i^* = c_{ia}^*\chi_{ia} + c_{ib}^*\chi_{ib}$$

The bond (bonding and antibonding) orbitals of each bond are obtained by the diagonalization of the 2×2 Fock matrix on the basis of the hybrid orbitals.[18] A set of bond orbitals are optimized to give the maximum value of the coefficient of the ground configuration. The electron delocalizations were estimated by the absolute values of the ratios of the coefficients of the transferred configurations to the ground configuration (|CT/CG|).[2] In order to estimate the interaction of the bond orbitals, ϕ_i and ϕ_j, we calculate the interbond energy IBE_{ij}[17]

$$IBE_{ij} = P_{ij}(F_{ij} + H_{ij})$$

where P_{ij}, F_{ij}, and H_{ij} are the elements of the density, Fock, and core Hamiltonians, respectively.
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