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Orbital phase control of the conformations of α- and β-substituted enamines and vinyl ethers*

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Abstract. The conformational stabilities of the α- and β-substituted enamines and vinyl ethers were predicted by orbital phase theory and confirmed by ab initio molecular orbital calculations. Cyclic interaction significantly occurs among the nonbonding orbital n_Y for the lone pair on the hetero atom Y (N in the enamines or O in the ethers), the π and π* orbitals of the C=C bond, and the $\sigma_{C\text{-}H}$ or $\sigma^*_{C\text{-}X}$ orbitals on the substituent CH_2X. The cyclic -n_Y-π-$\sigma_{C\text{-}H}$-π*- interaction is favored by the orbital phase continuity in the α-substituted molecules, while the cyclic -n_Y-π-$\sigma^*_{C\text{-}X}$-π*- interaction is favored in the β-substituted molecules. The most stable conformation was then predicted to be synperiplanar or (pseudo)equatorial in the α-substituted molecules and anticlinical or (pseudo)axial in the β-substituted molecules.

Key words: Orbital phase – Conformation – Enamine – Vinyl ether

1 Introduction

Cyclic orbital interactions were previously shown [1] to be involved even in acyclic conjugations. It follows that 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 conjugated isomers with both closed- [1, 2] and open-shell [3] electronic structures, to the regioselectivities of organic reactions [4], and to the abnormally acute coordinate angle of metal complexes [5].

In this paper we describe the significance of the orbital phase property in molecular conformations. The relative stabilities of the conformations of α- and β-substituted enamines and vinyl ethers are predicted by the orbital phase theory and confirmed by ab initio molecular orbital calculations.

2 Orbital phase predictions

2.1 Cyclic orbital interaction

There are two typical conformations of α- and β-substituted enamines and vinyl ethers (Fig. 1). In the synperiplanar (sp) conformation the electron-donating allylic C-H bonds interact with the π bond. In the anticlinal (ac) conformation the C-X bond preferentially interacts with the π bond. In the present work the substituent X is electron withdrawing.

The mechanism of the delocalization and polarization in the sp conformation is schematically represented in Fig. 2a. A pair of electrons occupies each of the n_Y orbitals, the π orbital, and the $\sigma_{C\text{-}H}$ orbital in the ground configuration (G). Electrons delocalize from the lone pair of the heteroatom to the π bond. This is expressed by the interaction of G with the transferred configuration (T_1), where an electron in n_Y shifts to the π* orbital. The G-T_1 configuration interaction is approximated by the n_Y-π* orbital interaction. The resulting electron hole in the n_Y orbital is supplied with an electron by the π orbital through the interaction of T_1 with the locally excited configuration (E), where one electron is promoted from π to π*. The mixing of the excited configuration polarizes the π bond. The T_1-E interaction is approximated by the π-n_Y interaction. The G-T_1-E or π-n_Y-π* interaction is involved in the delocalization-polarization process. The process through the $\sigma_{C\text{-}H}$ orbital in place of the n_Y orbital similarly involves the G-T_2-E or π-$\sigma_{C\text{-}H}$-π* interaction. As a result, the cyclic -G-T_1-E-T_2- or -n_Y-π-$\sigma_{C\text{-}H}$-π*- interaction (Fig. 3a) occurs.

The delocalization-polarization mechanism in the ac conformation is shown in Fig. 2b. The lone pair electron delocalizes to the π bond through the G-T_1 or n_Y-π* interaction. The π bond polarizes through the T_1-E interaction or π-n_Y interaction. The G-T_1-E or π-n_Y-π*

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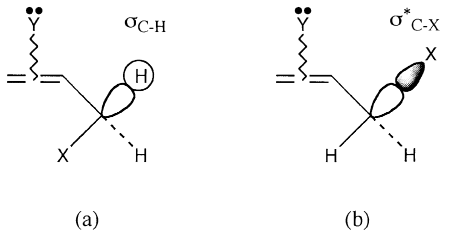
interaction is involved in the delocalization-polarization process. The polarization through the $\sigma^*_{C\text{-}X}$ orbital involves the G-T_3-E or π-$\sigma^*_{C\text{-}X}$-π^* interaction. As a result, the cyclic -G-T_1-E-T_3- or -n_Y-π-$\sigma^*_{C\text{-}X}$-π^*- interaction (Fig. 3b) occurs. The cyclic orbital interaction is also involved in the distant delocalization from the n_Y orbital to the $\sigma^*_{C\text{-}X}$ orbital via the π and π^* orbitals (Fig. 2b). The electron in the π^* orbital T_1 further shifts to the $\sigma^*_{C\text{-}X}$ orbital through the interaction of T_1 with another transferred configuration T_4 or through the π^*-$\sigma^*_{C\text{-}X}$ interaction. The electron hole in the π orbital in T_3 is supplied with an electron by the n_Y orbital through the interaction with T_4 or through the n_Y-π interaction. The cyclic -G-T_1-T_4-T_3- or -n_Y-π-$\sigma^*_{C\text{-}X}$-π^*- interaction (Fig. 3b) occurs.



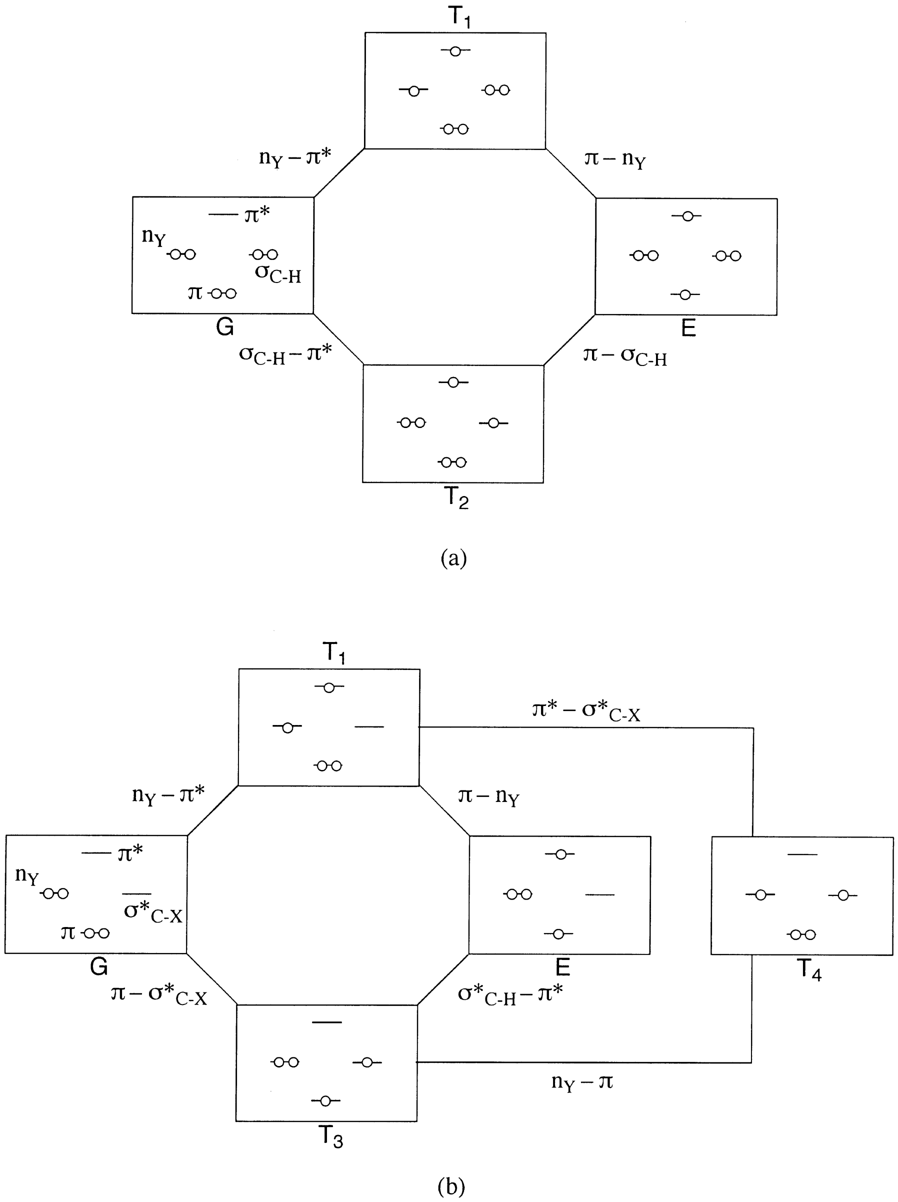
(a) (b)

Fig. 1. **a** sp and **b** ac conformations of substituted enamines and vinyl ethers

2.2 Orbital phase continuity

Cyclic orbital interactions are required for effective occurrence to meet the following conditions [1]: (1) the bonding or nonbonding (occupied) orbitals are out of phase; (2) the antibonding (unoccupied) orbitals are in phase; and (3) the bonding (nonbonding) and antibond-

Fig. 2a,b. Delocalization-polarization mechanisms of **a** the sp and **b** the ac conformations



ing 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 interaction does not effectively contribute to stabilization.

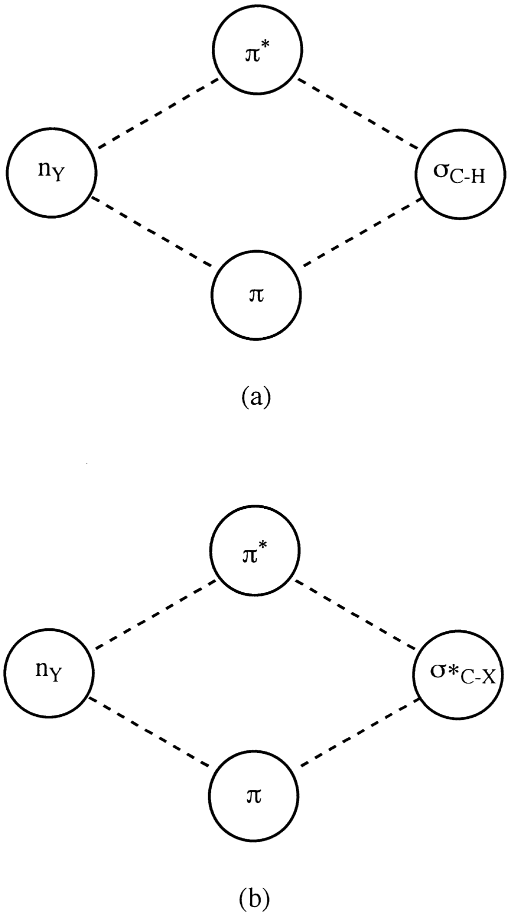


Fig. 3a,b. Cyclic orbital interactions significant in the **a** sp and **b** ac conformations

The stable conformer of the α-substituted molecules was predicted from the orbital phase continuity to be sp. The phase of the -n_Y-π-$\sigma_{C\text{-}H}$-π^*- orbitals in the α-substituted molecules is continuous (Fig. 4a): the donating π and n_Y orbitals are out of phase; the π and $\sigma_{C\text{-}H}$ orbitals are out of phase; the n_Y and π^* orbitals are in phase; and the $\sigma_{C\text{-}H}$ and π^* orbitals are in phase. The orbital phase for the cyclic interaction involving the $\sigma^*_{C\text{-}X}$ orbital in place of the $\sigma_{C\text{-}H}$ orbital is discontinuous (Fig. 4b).

For the β-substituted molecules, the ac conformers were predicted to be more stable. The -n_Y-π-$\sigma^*_{C\text{-}X}$-π^*- orbital phase is continuous (Fig. 4c): the n_Y and π orbitals are out of phase; the n_Y and π^* orbitals are in phase; the π and $\sigma^*_{C\text{-}X}$ orbitals are in phase; and the π^* and $\sigma^*_{C\text{-}X}$ orbitals are in phase. The orbital phase for the cyclic interaction involving the $\sigma_{C\text{-}H}$ orbital in place of the $\sigma^*_{C\text{-}X}$ orbital is discontinuous (Fig. 4d).

2.3 Numerical confirmation

The orbital phase continuity enhances the delocalizations and the polarizations. The method for estimating the delocalization and the polarization was previously described [6]. The single Slater determinant Ψ for the electron structure of the ground state is expanded into electron configurations:

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

The bonding and antibonding orbitals ϕ_i and $\phi_i{}^*$ of the ith bond are expressed by a linear combination of hybrid atomic orbitals χ_{ia} and χ_{ib} on bonded atoms:

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

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

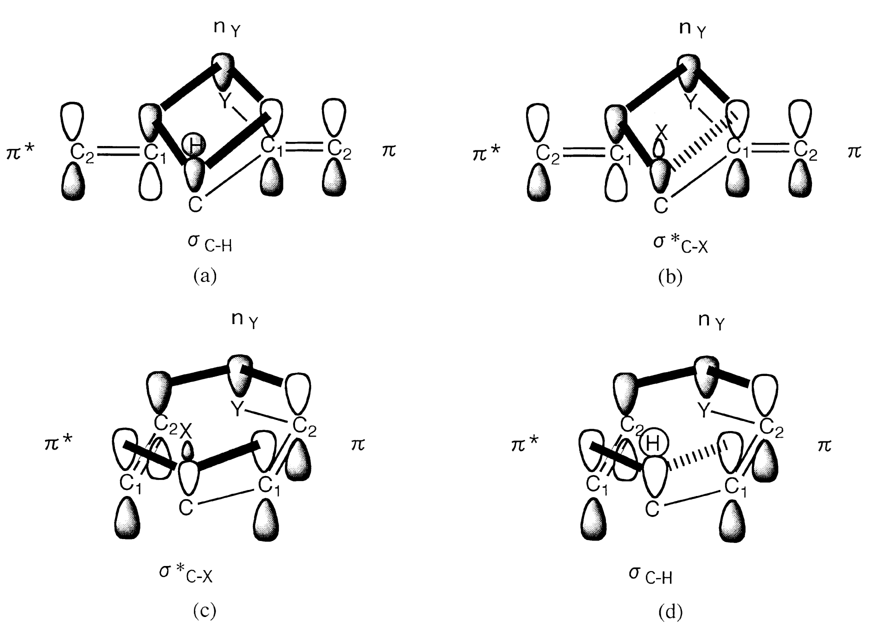
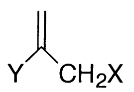
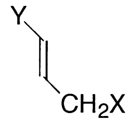


Fig. 4a–d. Orbital phase properties in the α- and β-substituted enamines and vinyl ethers



1a X=F, Y=OH
2a X=F, Y=NH$_2$
3a X=F, Y=CH$_3$
4a X=Cl, Y=OH
5a X=Cl, Y=NH$_2$
6a X=Cl, Y=CH$_3$



1b X=F, Y=OH
2b X=F, Y=NH$_2$
3b X=F, Y=CH$_3$
4b X=Cl, Y=OH
5b X=Cl, Y=NH$_2$
6b X=Cl, Y=CH$_3$

The hybrid atomic orbitals are optimized to maximize the value of the coefficient (C_G) of the ground configuration [6]. The electron delocalizations from bonds to bonds and the bond polarizations were estimated by the absolute values of the ratios of the coefficients of the transferred and the locally excited configurations to that of the ground configuration (C_T/C_G and C_E/C_G) [2].

We optimized the geometries of the model molecules **1** (X = F, Y = OH) and **4** (X = Cl, Y = OH) by ab initio molecular orbital calculations at the RHF/6-31G* level [7]. We used the minimal basis set to estimate the delocalizations and the polarizations. The calculated orbital energies of the π and $\sigma_{C\text{-}X}$ bonds supported the assumption that the $\sigma^*_{C\text{-}X}$ orbital rather than the $\sigma_{C\text{-}X}$ orbital significantly participates in the cyclic interaction. For example, the energy gaps of the π and $\sigma^*_{C\text{-}X}$ orbitals (0.753 au, 0.254 au) were smaller than the π^* and $\sigma_{C\text{-}X}$ orbitals (1.447 au, 1.308 au) in the ac conformers of **1a** and **4a**, respectively.

The orbital phase predictions were confirmed by the delocalizations and the polarizations (Table 1). For the α-substituted molecules (**1a** and **4a**), the $\pi \rightarrow \pi^*$ polarizations occurred in the sp conformers (0.034 and 0.034) to greater extent than in the ac conformers (0.031 and 0.033), as expected from the orbital phase continuity of the cyclic -n_O-π-$\sigma_{C\text{-}H}$-π^*- interaction involving the polarization in the sp conformation. The polarizations induce the $n_O \rightarrow \pi^*$ delocalizations in the sp conformers (0.261 and 0.257) more than in the ac conformers (0.245 and 0.247). For the β-substituted molecules (**1b** and **4b**), the $\pi \rightarrow \pi^*$ polarizations were found to occur to greater extent in the ac conformers (0.006 and 0.003) than in the sp conformers (0.002 and 0.001), in agreement with the phase continuity of the -n_Y-π-$\sigma^*_{C\text{-}X}$-π^*- orbitals. The $n_O \rightarrow \sigma^*_{C\text{-}X}$ distant delocalizations (0.023 and 0.037) are appreciable in the ac conformers, as predicted from the orbital phase property. The bond polarizations and the distant delocalizations enhance the $n_O \rightarrow \pi^*$ delocalizations in the ac conformers (0.275 and 0.282) more than in the sp conformers (0.270 and 0.275).

Table 1. The electron delocalization[a] from bonds to bonds and the polarizations[a] of bonds in the conformers of **1a**, **1b**, **4a**, and **4b**

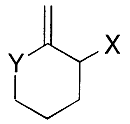
		1a	
Conformation	$\pi \rightarrow \pi^*$	$n_O \rightarrow \pi^*$	$n_O \rightarrow \sigma^*_{CF}$
sp	0.034	0.261	0.000
ac	0.031	0.245	0.001
		1b	
	$\pi \rightarrow \pi^*$	$n_O \rightarrow \pi^*$	$n_O \rightarrow \sigma^*_{CF}$
sp	0.002	0.270	0.000
ac	0.006	0.275	0.023
		4a	
	$\pi \rightarrow \pi^*$	$n_O \rightarrow \pi^*$	$n_O \rightarrow \sigma^*_{CCl}$
sp	0.034	0.257	0.000
ac	0.033	0.247	0.006
		4b	
	$\pi \rightarrow \pi^*$	$n_O \rightarrow \pi^*$	$n_O \rightarrow \sigma^*_{CCl}$
sp	0.001	0.275	0.000
ac	0.003	0.282	0.037

[a] Indicated by the absolute values of the coefficient ratios ($|C_T/C_G|$ and $|C_E/C_G|$)

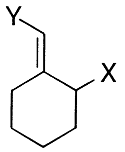
3 Conformational stabilities

The stable conformers of the α-substituted enamines and vinyl ethers were predicted from the orbital phase theory to be sp in the acyclic molecules. The orbital phase theory was readily applied to the cyclic molecules (**7**, **8**, **13**, and **14**). The sp conformations in the acyclic molecules correspond to the (pseudo)equatorial conformations where the C—H bond preferentially interacts with the π bond. The predictions were confirmed by the calculated relative stabilities of most of the fluoro derivatives (**1a**, **2a**, **7a**, **8a**, and **14a**) examined (Table 2). The relative instability of the pseudoequatorial conformer of **13a** results possibly from the repulsion of the lone pairs on the F and O atoms close to each other.

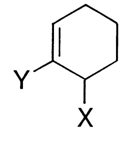
The most stable conformers of the β-substituted molecules were predicted from the orbital phase theory to be ac in the acyclic molecules and (pseudo)axial in the cyclic molecules. The predictions were completely confirmed by the calculated relative stabilities of all the



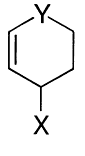
7a X=F, Y=O
8a X=F, Y=NH
9a X=F, Y=CH$_2$
10a X=Cl, Y=O
11a X=Cl, Y=NH
12a X=Cl, Y=CH$_2$



7b X=F, Y=OH
8b X=F, Y=NH$_2$
9b X=F, Y=CH$_3$
10b X=Cl, Y=OH
11b X=Cl, Y=NH$_2$
12b X=Cl, Y=CH$_3$



13a X=F, Y=OH
14a X=F, Y=NH$_2$
15a X=F, Y=CH$_3$
16a X=Cl, Y=OH
17a X=Cl, Y=NH$_2$
18a X=Cl, Y=CH$_3$



13b X=F, Y=O
14b X=F, Y=NH
15b X=F, Y=CH$_2$
16b X=Cl, Y=O
17b X=Cl, Y=NH
18b X=Cl, Y=CH$_2$

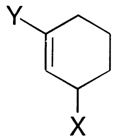
Table 2. The total energies (in au), the relative energies ΔE (in kcal/mol) and the corrected relative stabilities ΔE_T (in kcal/mol) by reference molecules of the conformers of **1**–**24**

Molecule	Total energies		ΔE[a]	ΔE_T[b]	Molecule	Total energies		ΔE[a]	ΔE_T[b]
	sp (or (pseudo)eq	ac or (pseudo)ax				sp or (pseudo)eq	ac or (pseudo)ax		
1a	−290.77691	−290.77394	−1.86	−1.87	**1b**	−290.77252	−290.77338	0.54	0.78
2a	−270.94735	−270.94619[c]	−1.71	−1.72	**2b**	−270.94677	−270.94774	0.61	0.85
3a	−254.95694	−254.95695	0.01	0.00	**3b**	−254.95713	−254.95674	−0.24	0.00
4a	−650.82788	−650.82863	0.47	−0.89	**4b**	−650.82417	−650.82790	2.34	0.69
5a	−630.99850	−630.99978[c]	0.80	−0.56	**5b**	−630.99873	−631.00261	2.44	0.79
6a	−615.00847	−615.01066	1.36	0.00	**6b**	−615.00916	−615.01178	1.65	0.00
7a	−406.71954	−406.71782	−1.08	−0.93	**7b**	−445.76068	−445.76196	0.81	0.65
8a	−386.89483	−386.89260	−1.40	−1.25	**8b**	−425.93450	−425.93556	0.67	0.51
9a	−370.90851	−370.90828	−0.15	0.00	**9b**	−409.94420	−409.94446	0.16	0.00
10a	−766.76719	−766.76790	0.44	−0.67	**10b**	−805.80742	−805.81130	2.43	0.55
11a	−746.94182	−746.94253	0.45	−0.66	**11b**	−785.98160	−785.98536	2.36	0.48
12a	−730.95606	−730.95782	1.11	0.00	**12b**	−769.99093	−769.99392	1.88	0.00
13a	−406.72710	−406.72877	1.05	1.13	**13b**	−367.68527	−367.68737	1.32	1.42
14a	−386.90416	−386.90315	−0.63	−0.55	**14b**	−347.85928	−347.86152	1.41	1.51
15a	−370.91222	−370.91210	−0.08	0.00	**15b**	−331.87303	−331.87286	−0.10	0.00
16a	−766.77682	−766.77935	1.59	0.42	**16b**	−727.73616	−727.73792	1.10	0.94
17a	−746.95251	−746.95363	0.71	−0.46	**17b**	−707.91034	−707.91245	1.32	1.16
18a	−730.96253	−730.96067	1.17	0.00	**18b**	−691.92389	−691.92415	0.16	0.00
					19b	−406.73341	−406.73443	0.64	0.63
					20b	−386.90471	−386.90605	0.84	0.83
					21b	−370.91259	−370.91261	0.01	0.00
					22b	−766.78391	−766.78492	0.63	0.36
					23b	−746.95544	−746.95691	0.92	0.65
					24b	−730.96344	−730.96386	0.27	0.00

[a] ΔE = (sp or (pseudo) eq − (ac or (pseudo)ax)

[b] $\Delta E_T = \Delta E_{\text{corresponding molecule}} - \Delta E_{\text{reference molecule}}$

[c] Another anticlinal conformer where the amino nitrogen is pyramidalized in the opposite direction is the most stable, possibly owing to hydrogen bonding between the N-H bond and the C-F (C-Cl) bond



19b X=F, Y=OH
20b X=F, Y=NH_2
21b X=F, Y=CH_3
22b X=Cl, Y=OH
23b X=Cl, Y=NH_2
24b X=Cl, Y=CH_3

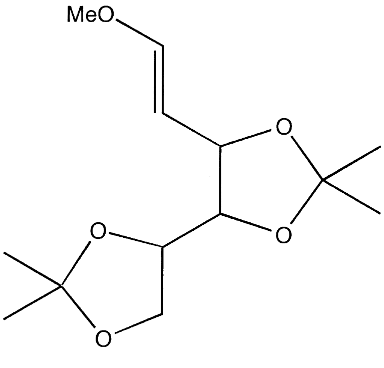
fluoro derivatives (**1b**, **2b**, **7b**, **8b**, **13b**, **14b**, **19b**, and **20b**). The orbital phase predictions were in good agreement with the experimental observations [8, 9]. Tronchet and Xuan [8] concluded that the ac conformations of the glycenoses (e.g. **25**) and alkenes having the general formula RCH(OR)CH = CHX are favored when X is an electron donating group. An NMR study [9] of **26** and **27** showed that the methoxy group at the β-position increases the portion of the pseudoaxial conformers of the cyclohexenes with a hydroxy or methoxy group at the allylic position. A similar effect of the methoxy group was observed for the methylenecyclohexane derivatives **28**.

In the chloro derivatives of the α-substituted molecules (**4a**, **5a**, **10a**, **11a**, **16a**, and **17a**), the calculated relative stabilities were in disagreement with the predictions that the sp or (pseudo)equatorial conformations should be more stable. The disagreement results from the strong preference of allyl chloride itself for the ac conformation [10]. We calculated the preference of the ac conformations of the reference molecules (**6a**, **12a**, and **18a**), where the lone pairs on the heteroatom are replaced by C-H bonds. The calculations showed that the relative stabilities of the ac or (pseudo)axial conformers are greater in the reference molecules (**6a**, **12a**, and **18a**) than in the corresponding enamines and vinyl ethers. The results suggest that the sp or (pseudo)equatorial conformers should be stabilized by the orbital phase property, as has been predicted. The pseudoequatorial conformer of **16a** is still relatively unstable even if the relative conformational stability of the reference molecule is taken into account. This results possibly from the destabilization of the pseudoequatorial conformer owing to the repulsion of lone pairs on the Cl and O atoms (see the above discussion about **13a**).

The calculated relative stabilities of the conformers of the β-substituted chloro derivatives (**4b**, **5b**, **10b**, **11b**, **16b**, **17b**, **22b**, and **23b**) completely confirmed the predictions that the ac or (pseudo)axial conformations should be more stable.

Among the interesting related subjects are the conformational stabilities of dimethoxyethylenes (**29**). The methoxy group can be an electron donor toward the π bond in the periplanar conformation where an n_O orbital of oxygen atom significantly interacts with the π^* orbital. The methoxy group can also be an electron acceptor in the ac conformation where the $\sigma^*_{\text{O-Me}}$ orbital.

The stable conformers of 1,1-dimethoxyethylene **29a** were predicted by orbital phase theory to be sp or ac for both methoxy groups (Fig. 5a). Methyl vinyl ether itself assumes a sp conformation. The sp,sp conformer is the most stable (Fig. 6). The most stable conformer of 1,2-dimethoxyethylene **29b** was predicted to assume one methoxy group at the sp position and the other methoxy group at the ac position since the phase was continuous (Fig. 5c). The calculated relative stabilities (Table 3) confirmed the most stable conformer of **29a** was sp for both methoxy groups. The sp,ac conformation was not a local minimum. This is consistent with the discontinuous orbital phase. The calculations showed the preference for the sp,ac conformer of **29b**, in agreement with the orbital phase prediction. However, the relative stability is small owing to the strong tendency of vinyl ether itself toward the sp conformation.



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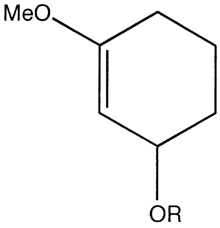
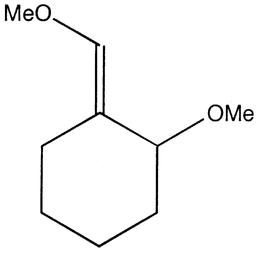


26 R=H
27 R=Me



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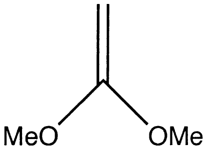
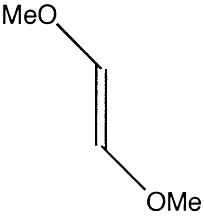


29a



29b

4 Conclusion

We have applied the orbital phase theory to the conformational stabilities of the α- and β-substituted enamines and vinyl ethers. For the α-substituted molecules, the $-n_{Y}-\pi-\sigma_{C-H}-\pi^{*}-$ orbital phase is continuous in the sp or (pseudo)equatorial conformation (Fig. 4a). The sp or (pseudo)equatorial conformers were predicted to be the most stable. The most stable conformers of the β-substituted molecules were predicted to be ac or (pseudo)axial where the $-n_{Y}-\pi-\sigma^{*}_{C-X}-\pi^{*}-$ orbital phase is continuous (Fig. 4c). The predictions were confirmed by

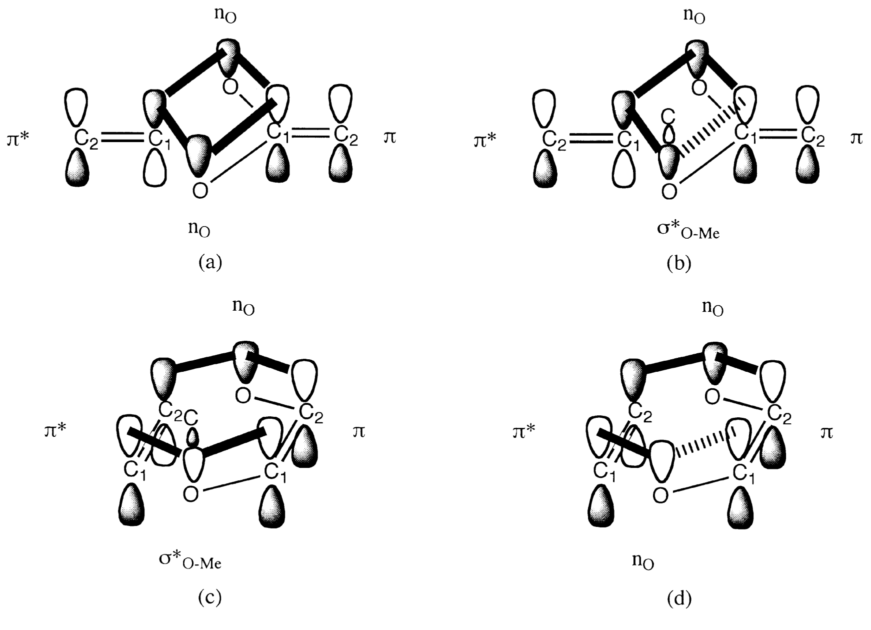


Fig. 5a–d. Orbital phase properties in the 1,1- and 1,2-dimethoxyethylenes

Table 3. The relative energies ΔE (in kcal/mol) of the conformers of **29**

Conformer	ΔE
29a	
sp, sp	−2.80
+ac, +ac	0.00
29b	
sp, ac	−0.50
+ac, −ac	−0.27
+ac, +ac	−0.20
sp, sp	0.00

the relative stabilities of the fluoro derivatives (**1**, **2**, **7**, **8**, **13**, **14**, **19**, and **20**) calculated by ab initio molecular orbital methods. In the chloro derivatives, the calculated relative stabilities were in good agreement with the prediction for the β-substituted molecules, but not for the α-substituted molecules. The disagreement of the α-substituted molecules was attributed to the strong preference of the allyl chloride moieties for ac conformations. The most stable conformers of 1,1- and 1,2-dimethoxyethylenes were predicted from the orbital phase theory and confirmed by the calculations to be the (sp,sp) and (sp,ac) conformers, respectively. Thus the orbital phase has been shown to control conformational stabilities.

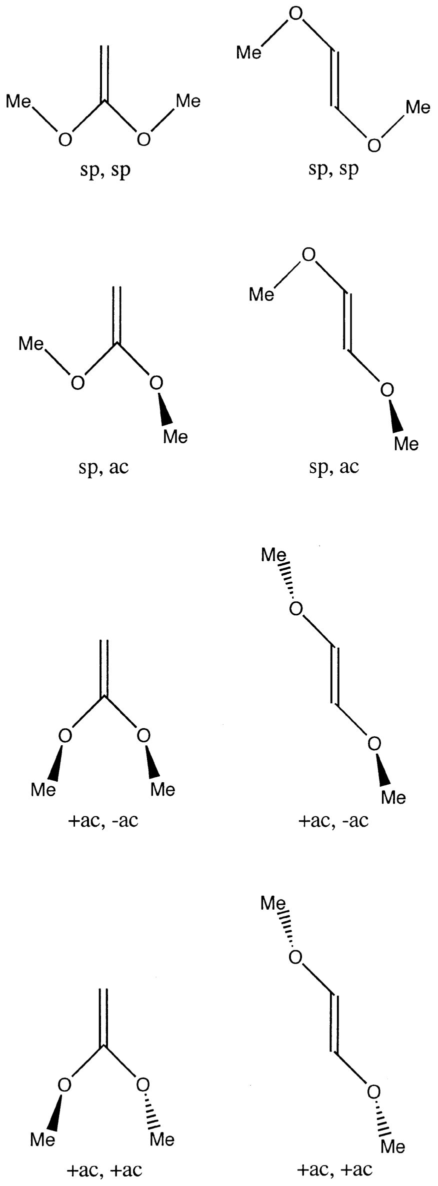


Fig. 6. Conformations of 1,1- and 1,2-dimethoxyethylenes

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