

Dynamic stability of carbonyl ylides

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The non- and fluorine-substituted singlet carbonyl ylides are studied by using ab initio MCSCF calculations. The thermodynamic stability of the carbonyl ylides and the intramolecular stability to isomerization or fragmentation reaction coordinates is demonstrated in terms of the topological structure of the ab initio potential energy surfaces. The allylic resonance is found to be dynamically unstable, considering out-of-plane vibrational mode. The instability is studied by the symmetries of the low-lying excitations out of the MCSCF wave function.

Key words: Carbonyl ylide — Allylic resonance — Second-order Jahn-Teller effect — Reaction coordinate — Frontier orbital

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1. Introduction

The studies on the structures of carbonyl ylides have formed an active area of chemical research because they are important intermediates in organic syntheses [1-3]. The ylide compounds in general are extremely difficult to be characterized both in terms of structures and in terms of energetics. Hence, a number of workers have recently studied the simple ylides including carbonyl ylides by using molecular orbital theory [1, 4-7]. There are three triplet states and three characteristic kinds of singlet states such as two of zwitterionic character and one of diradical character [8]. The relative stability of these states is considered a function of the substituents and of course solvent polarity [1]. The non-substituted carbonyl ylide is predicted to be a planar species which will rapidly invert about oxygen but only slowly rotate about the partial CO double bond [1]. The rotational process in $\text{H}_2\text{C}=\text{O}-\text{CH}_2$ has been one of the fundamental problems in the field of theoretical organic chemistry [1, 4-6]. The carbonyl ylides can react with methanol or a variety of multiple bonds: the 1,3-dipolar cycloadditions of carbonyl ylides to dipolarophiles have also been studied recently using accurate molecular orbital calculations [9, 10].

Carbonyl ylides can be formed by the thermolysis or photolysis of oxiranes or oxadiazolines or the addition of carbene to carbonyl compounds, and the most common reaction for the decay of carbonyl ylides is ring closure to form the corresponding oxirane [11]. Also, fragmentation to carbene and ketone can be induced either photochemically or thermally. In this connection, recently, a clear example of carbonyl ylide formation by reaction of a free carbene with a ketone has been reported using bulky substituents [12]. Subsequently, the demonstration of the reversible thermal fragmentation of a carbonyl ylide has been published [13]. These are recent clear examples of addition of a carbene to a ketone to yield an ylide where there is no ambiguity about whether the carbene is a free species or a metal-complexed carbenoid.

In the present paper, we shall give an attention to the out-of-plane motion of singlet carbonyl ylides and substituent effect to it, since the carbonyl ylide intermediate is likely to have a nonplanar structure [14] in particular in order for the ylide to fragment thermally to carbene and carbonyl compound [1, 15]. Allylic resonance is broken in the course of the out-of-plane motion. In this connection, Davidson et al. have recently discussed about the allylic resonance in formyloxyl, $\text{O}(\text{CH}_2)_2^+$, and $\text{O}(\text{CH}_2)_2$ by using ab initio MCSCF and CI calculations [16]. With the application of second-order Jahn-Teller theory [17], they showed that electronegativity differences and cyclic conjugation can each minimize the importance of allylic resonance in radicals. The reactions and lifetimes of the carbonyl ylides depend strongly on the nature of the substituents, particularly the structural deformations induced by the substituents. In most of theoretical studies, extremes of donor and acceptor substituents have been represented by standard amino and cyano groups, respectively [1]. It follows naturally that the effect of halogen as a substituent would be interesting to discuss because (1) it is frequently used in experiment, and (2) halogen has both donor

and acceptor character. Hence, in the present paper, the effect of fluorination to carbonyl ylide is also examined.

2. Method of calculation

Ab initio RHF molecular orbital calculations [18] with the split valence 4-31G basis set [19] are performed to determine the optimized geometries by using the energy gradient method [20]. The vibrational modes of the present species are analyzed. The second derivatives of the energy which are required for the vibrational analysis are obtained by the numerical differentiation of the analytical first derivatives [21]. In order to estimate more accurate energetical stability, we have performed the third-order Møller-Plesset perturbation (MP-3) calculations [22] with the 4-31G and the 6-31G** basis sets [23] at the RHF/4-31G optimized geometry. Moreover, two configurations MCSCF calculations [24] with the 4-31G basis set (TCSCF/4-31G) are performed in order to obtain more accurate optimized geometries and analyse the vibrational structure at these optimized geometries.

3. Results and discussions

3.1. Energetics and geometrical characteristics of ylides

The key of ylide geometry is shown in Fig. 1, and the geometrical parameters are shown in Table 1. If we replace H attached to C with F, then the distance between the C and O decreases and the other CO distance increases. This tendency becomes noticeable when two H's attached to the same C are replaced with two fluorines. The correlation effect of π electron by TCSCF treatment lengthens every CO distance and reduces the angle \sphericalangle COC but bears no considerable shortening of the terminal CC distance. This corresponds to the electron occupation of the antibonding π orbital of the C-O-C π bond which is vacant in the RHF treatment.

Figure 2 shows the MP-3 relative energies of the equilibrium points in the reaction where the carbonyl ylide is produced from carbonyl compound and carbene. Taking the electron correlation into consideration, carbonyl ylide is stabilized to a very large extent. Taking notice of the differences of energy between the carbonyl

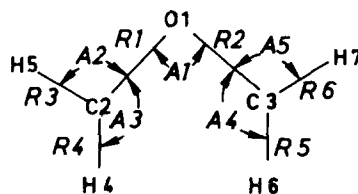


Fig. 1. The key of ylide geometry; R_i ($i = 1 \sim 6$) means bond lengths and A_j ($j = 1 \sim 5$) means bond angles

Table 1. The geometrical parameters of some carbonyl ylides optimized by RHF/4-31G (TCSCF/4-31G); R 's are bond lengths in angstroms and A 's are bond angles in degrees

	normal	H5 → F ^a	H4 → F ^a	H5, H6 → F ^a	H4, H5 → F ^a
R1	1.292 (1.333)	1.247 (1.308)	1.255 (1.308)	1.268 (1.318)	1.222 (1.294)
R2	1.292 (1.333)	1.320 (1.339)	1.314 (1.342)	1.276 (1.313)	1.353 (1.349)
R3	1.061 (1.062)	1.357 (1.357)	1.056 (1.056)	1.357 (1.353)	1.329 (1.335)
R4	1.067 (1.068)	1.060 (1.060)	1.365 (1.368)	1.057 (1.058)	1.336 (1.347)
R5	1.067 (1.068)	1.065 (1.067)	1.063 (1.064)	1.370 (1.366)	1.062 (1.064)
R6	1.061 (1.062)	1.059 (1.060)	1.059 (1.061)	1.053 (1.055)	1.057 (1.060)
R ₂₋₃ ^b	2.394 (2.420)	2.409 (2.422)	2.385 (2.412)	2.377 (2.405)	2.407 (2.411)
A1	135.8 (130.4)	139.6 (132.4)	136.4 (131.1)	138.3 (132.2)	138.3 (131.6)
A2	115.7 (115.2)	116.3 (114.6)	123.8 (123.2)	114.9 (113.7)	122.3 (121.0)
A3	119.4 (119.8)	126.4 (126.7)	117.0 (116.8)	125.8 (126.3)	122.8 (121.9)
A4	119.4 (119.8)	118.6 (119.8)	118.8 (119.6)	115.1 (115.9)	117.4 (119.2)
A5	115.7 (115.2)	114.5 (114.4)	114.4 (114.1)	123.4 (122.8)	112.9 (113.5)

^a Hi → F is the species substituted for Hi atom by fluorine

^b Bond length between C2 and C3 atoms

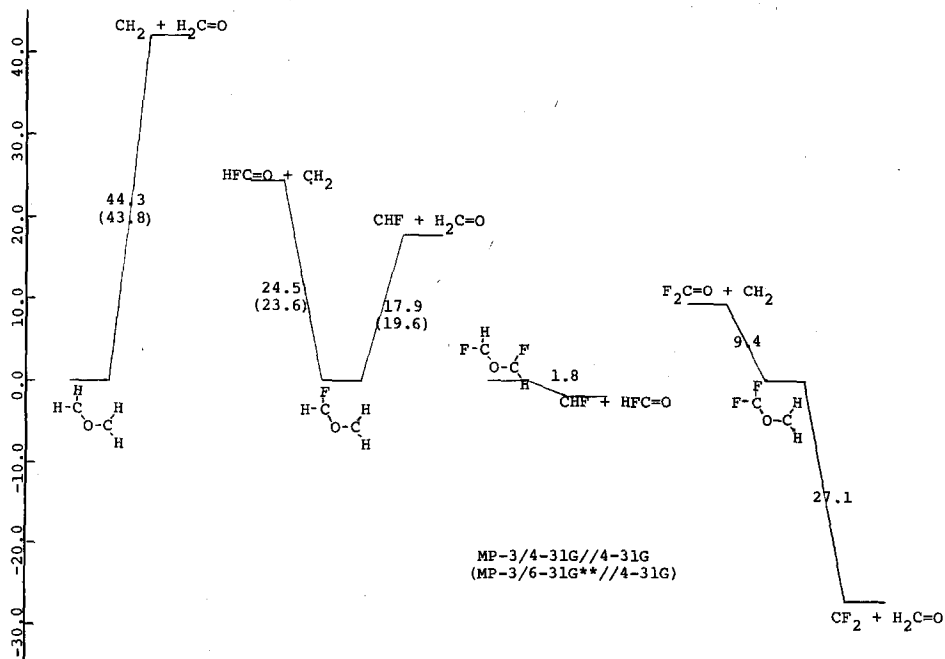


Fig. 2. The MP-3 relative energies of the equilibrium points calculated by MP-3/4-31G (6-31G**)//RHF/4-31G in kcal/mol

ylide and the constituent fragments, carbonyl ylides which are either non- or fluorine-substituted are more stable than the fragments. But the difluorocarbonyl ylides are unstable with respect to the fragmentation to fluorocarbene and formylfluoride, or to difluorocarbene and formaldehyde. As a matter of course, the reaction coordinates to ring closure are available for all the carbonyl ylides. The oxirane derivatives are the most stable products on the singlet potential energy surfaces.

The relative energy schemes of fluorine-substituted carbonyl ylides are shown in Fig. 3. The difference of total energy is compared for the model reactions (1)–(4). For the mono-substituted compounds, we have reactions (1) and (2). The enthalpy change of reaction (1) yielding the *cis* isomer is -6.5 kcal/mol, and that of reaction (2) yielding the *trans* isomer is -1.2 kcal/mol. The stable isomer takes the *cis* form as the product of reaction (1). The reason is that the fluorine in *cis* form can interact with the H6 hydrogen attached to C3, while the fluorine in *trans* form cannot interact with any hydrogens at the C3 site. This fluorine-hydrogen orbital interaction in *cis* form causes the reduction of A3 angle and C2–C3 bond length, as is shown in Table 1. This mechanism of stabilization is also shown in the difluorinated product of reaction (3) which has this fluorine-hydrogen orbital interaction. Although this fluorine-hydrogen orbital interaction works in the difluorinated product of reaction (4), the destabilization by fluorine

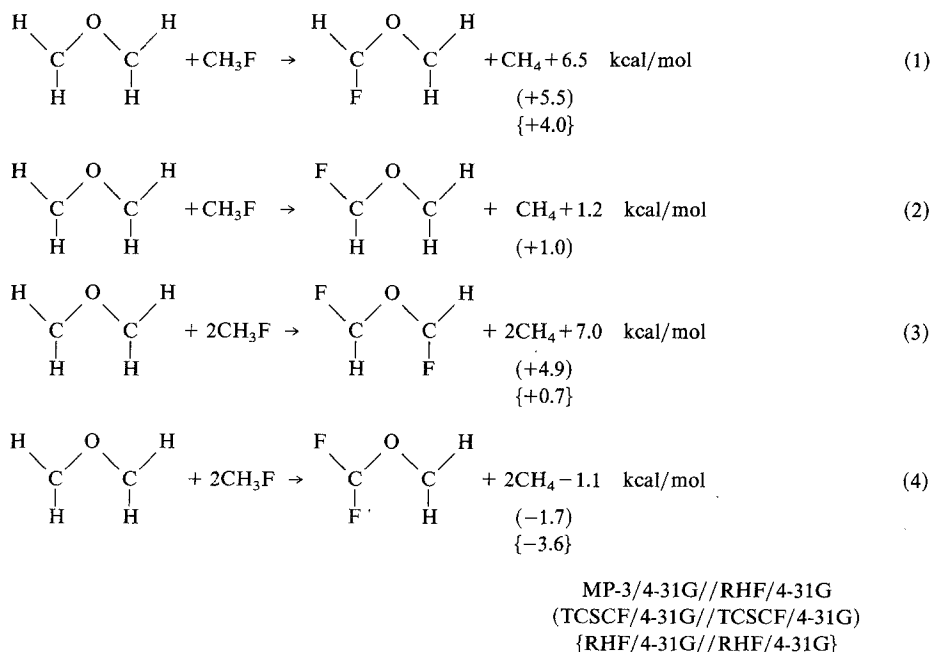


Fig. 3. The relative energy schemes of some fluorine-substituted carbonyl ylides. The heats of reaction are estimated by MP-3/4-31G//RHF/4-31G, TCSCF/4-31G//TCSCF/4-31G in parentheses and RHF/4-31G//RHF/4-31G in braces

substitution on the same carbon exceeds this stabilization by orbital interaction. Indeed, the enthalpy change of the reaction (4), 1.1 kcal/mol, shows that the structure in which two fluorines are substituted to the same carbon is not stable thermally.

3.2. The total atomic charges and gross orbital charges

The total atomic charges and the σ and π electron densities of the typical three carbonyl ylides are shown in Table 2. It is remarkable that the σ electron density at C3 decreases as $4.83 \rightarrow 4.31 \rightarrow 3.79$ e by mono- and di-substitution of fluorine. This is the effect of σ withdrawing of fluorine. On the other hand, the back-donation of π electron from the fluorine to the C-O-C π bond occurs: the total π electron density of the C-O-C bond increases as $4.00 \rightarrow 4.06 \rightarrow 4.12$ e. Also, reorganization of π electrons occurs at the terminal carbons. Indeed, the π electron at C3 decreases as $1.29 \rightarrow 1.20 \rightarrow 1.09$ e and the π electron at O1 remains almost unchanged, while the π electron at C2 increases as $1.26 \rightarrow 1.34 \rightarrow 1.49$ e.

As to the fluorine electron density, the σ electron density is rich compared with corresponding electron density of hydrogen, but the π electron density is less than 2.0, which is attributed to π back-donation.

Table 2. The total atomic charges and the σ and π electron densities of the typical three carbonyl ylides by RHF/4-31G

Structure 1: H6, H7-C3, O1-C2, H4, H5		Structure 2: F6, H7-C3, O1-C2, H4, H5		Structure 3: F6, F7-C3, O1-C2, H4, H5	
O1	8.52	O1	8.54	O1	8.54
σ	7.04	σ	7.02	σ	7.00
π	1.48	π	1.52	π	1.54
C2	6.09	C2	6.15	C2	6.23
σ	4.83	σ	4.81	σ	4.74
π	1.26	π	1.34	π	1.49
C3	6.09	C3	5.51	C3	4.88
σ	4.83	σ	4.31	σ	3.79
π	1.26	π	1.20	π	1.09
H4	0.84	H4	0.81	H4	0.82
H5	0.81	H5	0.81	H5	0.80
H6	0.84	F6	9.42	F6	9.37
		σ	7.48	σ	7.43
		π	1.94	π	1.94
H7	0.81	H7	0.76	F7	9.36
				σ	7.42
				π	1.94
$\pi(\text{COC})$	4.00		4.06		4.12

3.3. Stability of carbonyl ylides and the dynamical electronic processes

The vibrational analyses are performed for non-substituted and substituted carbonyl ylides by RHF/4-31G at the geometries shown in Fig. 1 and Table 1. For mono-substituted carbonyl ylides, only *cis* form is treated because it is the stable isomer as noted in Sect. 3.1. The normal vibrational frequencies corresponding to RHF normal vibrational modes for the structure of non-substituted carbonyl ylide have no imaginary values, so it shows that this structure is located at minimum on the potential energy surface. The structure of *cis*-fluorinated carbonyl ylide is also concluded to be a minimum point, but the least one of RHF normal vibrational frequencies is very small and this is out-of-plane vibrational mode. The structure of difluorinated carbonyl ylide in which H5 and H6 are substituted is concluded to be a transition state which has only one imaginary vibrational mode. This imaginary frequency is large relatively, which corresponds to out-of-plane imaginary vibrational mode. The structure of difluorinated carbonyl ylide in which H4 and H5 are substituted is very unstable and has two imaginary vibrational modes, and these two modes correspond to out-of-plane vibrational modes.

The results of vibrational analyses by TCSCF/4-31G at the TCSCF/4-31G geometries revealed that non-substituted carbonyl ylide has two imaginary frequencies which correspond to out-of-plane vibrational modes of symmetry a_2 and b_1 . The b_2 mode corresponding to the formation of the rotamer has positive force constant, which is in agreement with the work of Davidson et al. [16]. We also found that fluorinated carbonyl ylides have two imaginary out-of-plane vibrational modes of symmetry a'' which correspond to the a_2 and b_1 modes of non-substituted carbonyl ylide. These two out-of-plane imaginary modes of non-substituted carbonyl ylide are schematically shown in Fig. 4. Among these modes, b_1 mode corresponds to the direction of cyclization to form ethylene oxide. On the other hand, if we deform the carbonyl ylide along the a_2 mode, the most stable structure of carbonyl ylide having C_s symmetry can be obtained. The equilibrium geometry which is fully optimized assuming nonplanar structure is shown in Fig. 5. The stabilization energy for pyramidalization is 0.6 kcal/mol

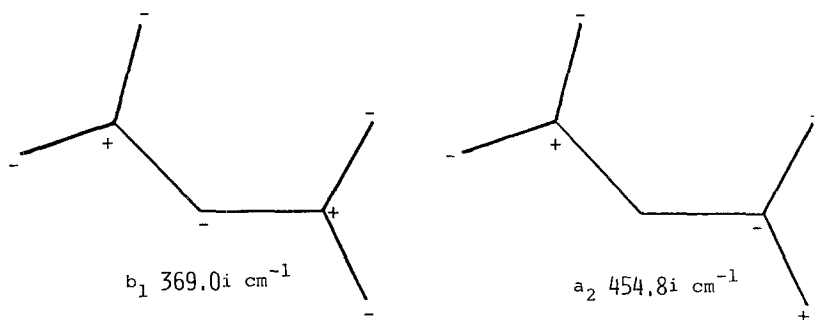


Fig. 4. The two out-of-plane imaginary vibrational modes of non-substituted carbonyl ylide by TCSCF/4-31G

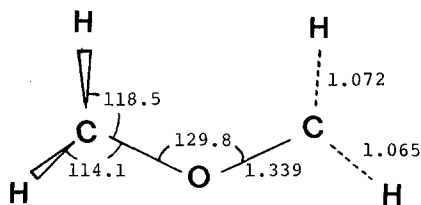


Fig. 5. The equilibrium geometry which is fully optimized assuming nonplanar structure by TCSCF/4-31G

which is well consistent with the MCSCF work by Davidson et al. [16]. Similarly the more stable structure of fluorinated carbonyl ylide may be optimized according to one of the a'' modes.

We apply second-order Jahn–Teller effect [7] to the electronic state described by TCSCF in order to investigate the main origin of the nonplanar shift in the stable structure. The symmetries of the mode which we treat are therefore a_2 and b_1 . The energy scheme on the basis of the Herzberg–Teller expansion is

$$E(Q_i) = E_0 + \frac{1}{2} \left\langle \Psi_0 \left| \left(\frac{\partial^2 H}{\partial Q_i^2} \right) \right| \Psi_0 \right\rangle + 2 \sum_{n \neq 0} \frac{|\langle \Psi_n | (\partial H / \partial Q_i) | \Psi_0 \rangle|^2}{E_0 - E_n} Q_i^2, \quad (1)$$

where Q_i is the coordinate of the i -th normal mode and the second term in the braces has always negative value for the electronic ground state ($E_n > E_0$). The matrix element in the problem is represented by using the transition density ρ_{0n} including the derivative of one-electron-operator u with respect to the normal coordinate Q_i :

$$\left\langle \Psi_n \left| \left(\frac{\partial H}{\partial Q_i} \right) \right| \Psi_0 \right\rangle = \int \rho_{0n} \left(\frac{\partial u}{\partial Q_i} \right) d\mathbf{v}, \quad (2)$$

$$\rho_{0n} = N \int \Psi_0^* \Psi_n d\tau', \quad (3)$$

where $d\mathbf{v}$ and $d\tau'$ denote the one-electron volume element and the complementary volume element in the N -electron system, respectively. Therefore, the major electronic process of the unstable normal modes of a_2 and b_1 symmetry should be governed by the dynamic access to the lowest excited states of a_2 and b_1 symmetry, respectively. The possible electronic excited states are easily found by the analysis of the frontier orbitals. The TCSCF ground state wavefunction Ψ_0 is represented by two configurations:

$$\Psi_0 = c_1 \psi_1 + c_2 \psi_2, \quad (4)$$

$$\psi_1 = \| \cdots (6a_1)^2 (1a_2)^2 (2b_1)^0 (7a_1) \cdots \|, \quad (5)$$

$$\psi_2 = \| \cdots (6a_1)^2 (2b_1)^2 (1a_2)^0 (7a_1) \cdots \|, \quad (6)$$

The corresponding lowest one-electron excitations are twofold. First, from ψ_1 ,

we may have the configuration of a_2 symmetry:

$$\Psi_n \cong \psi_{a_2}, \quad (7)$$

$$\psi_{a_2} = \left\| \cdots (6a_1)^2 (1a_2)^1 (7a_1)^1 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) (2b_1)^0 \cdots \right\|. \quad (8)$$

Secondly, from ψ_2 , we may have the configuration of b_1 symmetry:

$$\Psi_n \cong \psi_{b_1}, \quad (9)$$

$$\psi_{b_1} = \left\| \cdots (6a_1)^2 (2b_1)^1 (7a_1)^1 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) (1a_2)^0 \cdots \right\|, \quad (10)$$

and, again from ψ_1 ,

$$\psi_{b_1} = \left\| \cdots (1a_2)^2 (6a_1)^1 (2b_1)^1 \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) (7a_1)^0 \cdots \right\|. \quad (11)$$

Thus, the transition density ρ_{on} of the appropriate symmetry is obtained, and

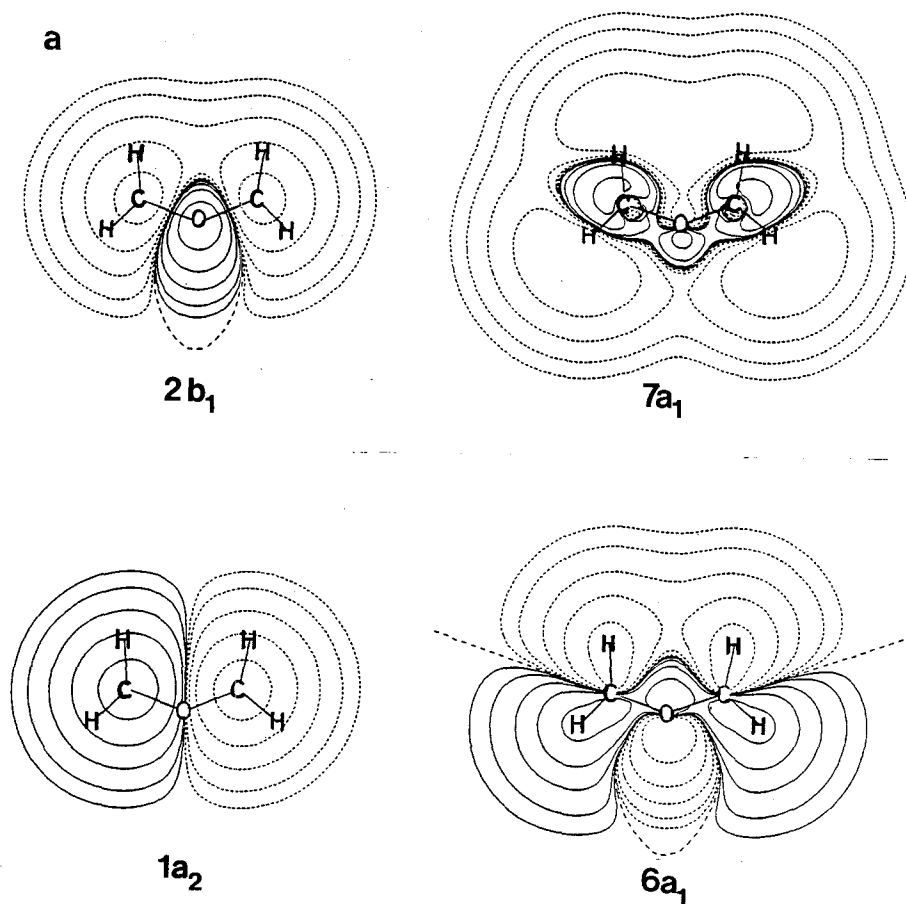


Fig. 6. a-c. The phase patterns of the frontier orbitals of three typical carbonyl ylides by RHF/4-31G. a Non-substituted carbonyl ylide; b *cis*-fluorinated carbonyl ylide; c difluorocarbonyl ylide

hence, the corresponding dynamic instability of carbonyl ylides will be brought about.

The orbital phase patterns of the frontier orbitals of non-substituted carbonyl ylides are drawn in Fig. 6(a). The combinations of the orbitals mentioned above correspond to $(1a_2 \times 7a_1)$, $(2b_1 \times 7a_1)$, and $(6a_1 \times 2b_1)$ in this figure. The corresponding frontier orbital phase patterns of fluorinated carbonyl ylides are shown in Fig. 6(b), (c), too. The movements for the out-of-plane mode are obtained by the products of phases of these frontier orbitals.

In Table 3, we show that the symmetry raised up by a combination between frontier orbitals of TCSCF corresponds to the imaginary vibrational mode. The two a'' modes of fluorinated carbonyl ylides are equivalent to a_2 or b_1 modes of non-substituted carbonyl ylide. In these ways, we have found that the dynamic instability of carbonyl ylides is understood by using the phase of frontier orbitals.

b

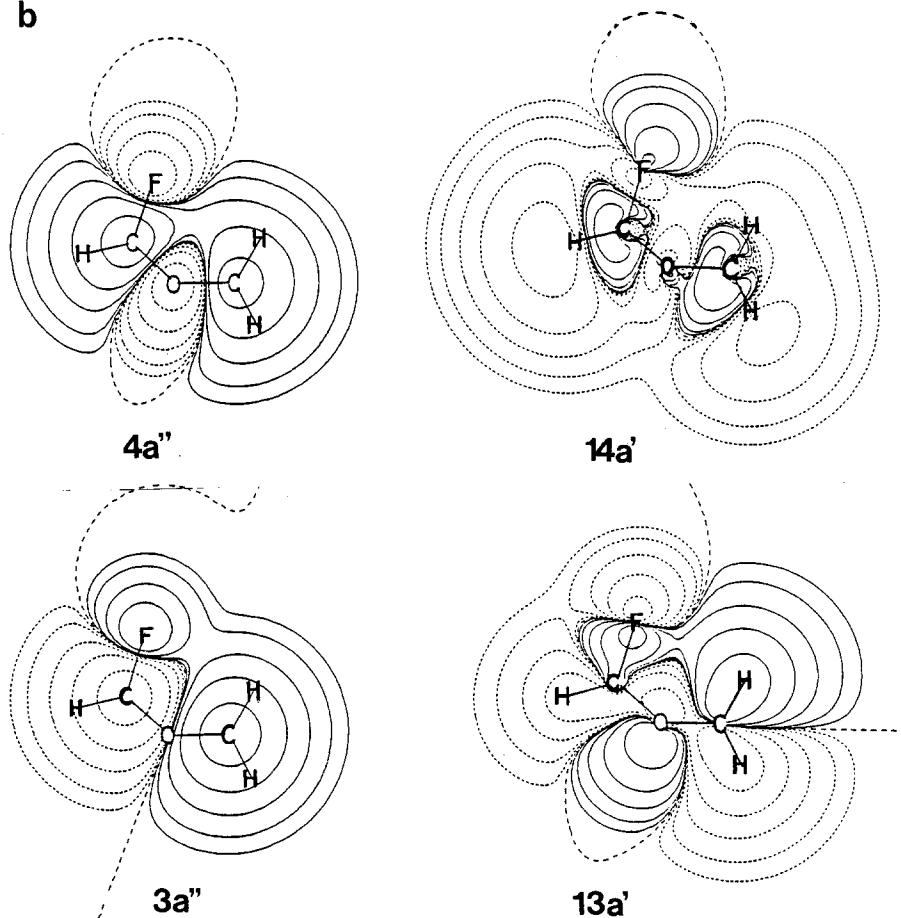


Fig. 6 (continued)

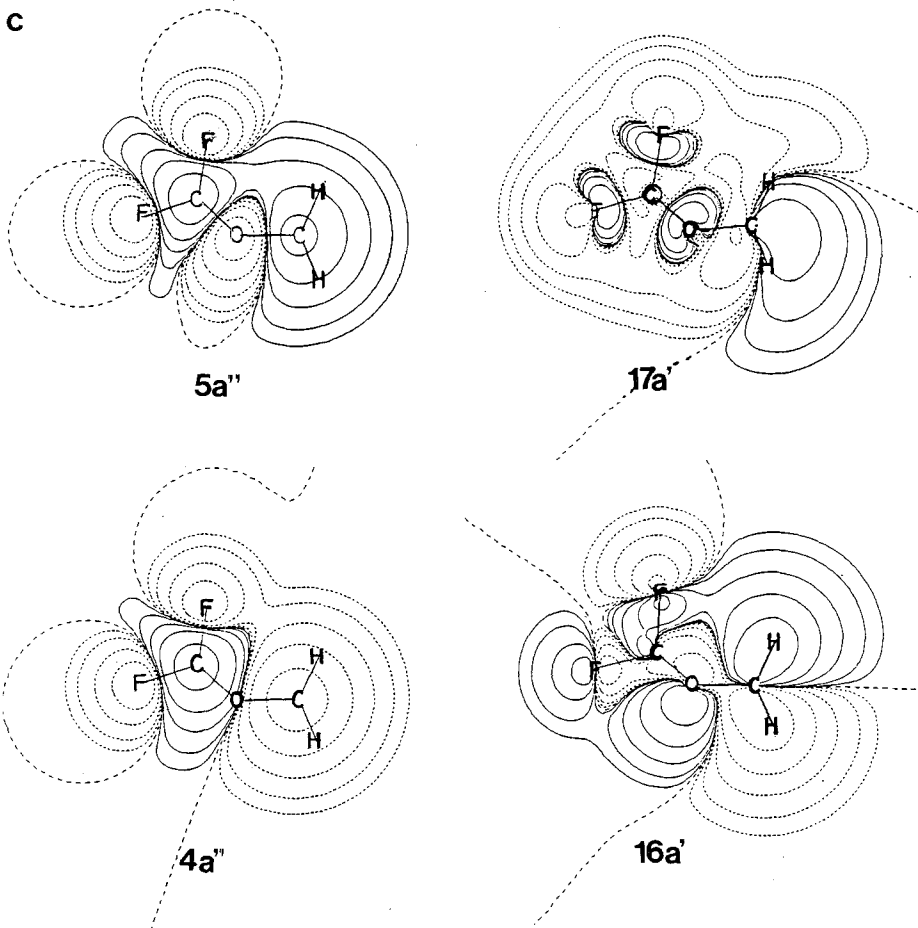


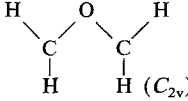
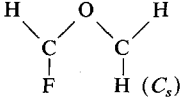
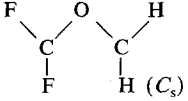
Fig. 6 (continued)

It should be noted that along the reaction coordinate to the formation of edge-to-face (EF) rotamer, the configuration corresponding to the combination of $(1a_2 \times 2b_1)$ should play an important role. For the dynamical processes along this reaction coordinate of b_2 symmetry, the coupling with the soft vibrational modes of a_2 and b_1 symmetry may play an important role, because the latter are candidates of the orthogonal vibrational modes which contribute to the instability of the reaction coordinate [25, 26].

4. Conclusion

The structure and electronic state of carbonyl ylide were investigated by second-order Jahn-Teller effect from the dynamic view point of chemical reaction systems. It is shown by MCSCF treatment that the characteristic displacement of nuclei from equilibrium structure can be understood in terms of the phase combination of frontier orbitals. In addition to the concept of allylic resonance which is usually

Table 3. The symmetry by a combination between frontier orbitals of TCSCF corresponding to the imaginary vibrational mode

Species (symmetry)	C_i^a	Electron configuration of ψ_i	Symmetry combination
 (C_{2v})	-0.899	$\psi_1 = \parallel \dots (6a_1)^2(1a_2)^2(2b_1)^0(7a_1)^0 \dots \parallel$	$1a_2 \times 7a_1 = a_2$
	0.438	$\psi_2 = \parallel \dots (6a_1)^2(2b_1)^2(1a_2)^0(7a_1)^0 \dots \parallel$	$6a_1 \times 2b_1 = b_1$ $2b_1 \times 7a_1 = b_1$
 (C_s)	-0.900	$\psi_1 = \parallel \dots (13a')^2(3a'')^2(4a'')^0(14a')^0 \dots \parallel$	$3a'' \times 14a' = a''$
	0.436	$\psi_2 = \parallel \dots (13a')^2(4a'')^2(3a'')^0(14a')^0 \dots \parallel$	$13a' \times 4a'' = a''$ $4a'' \times 14a' = a''$
 (C_s)	-0.897	$\psi_1 = \parallel \dots (16a')^2(4a'')^2(5a'')^0(17a')^0 \dots \parallel$	$4a'' \times 17a' = a''$
	0.442	$\psi_2 = \parallel \dots (16a')^2(5a'')^2(4a'')^0(17a')^0 \dots \parallel$	$16a' \times 5a'' = a''$ $5a'' \times 17a' = a''$

^a The expansion coefficient of Ψ_0 by ψ_i ($i = 1, 2$) in Eq. (4)

used to discuss the stability in a plane, we have focused on the dynamic instability with respect to the freedom of out-of-plane. And this can closely correspond to the experimental fact about the stability and the reactivity of ylide itself. The displacement of nuclei can favorably occur in the direction of the normal mode in phase with the combination of frontier orbitals. The substitution effect of fluorine on the stability of carbonyl ylide was also examined. The disubstituted ylides are thermodynamically unstable with respect to fragmentation. Thus, this study using MCSCF gives the important suggestion to the out-of-plane displacement of nuclei. This is in good agreement with experimental results [15]. Therefore, the present report is considered a basic building block for the determination of the real dynamically stable form of carbonyl ylides. Further progress of similar investigation is expected in future.

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