The Study of HOMO Energy for Showing the Basicity and the ν(C=O) Stretching Bands Obtained by the Semi-Empirical and *ab initio* Methods in Phosphorus Ylides

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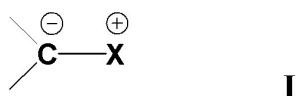Relationships between the HOMO energy, the ν(C=O) stretching band, basicity(pKa), and σ(p) in phosphorus ylides have been studied. A linear relationship between the HOMO energies obtained by the AM1, HF/3-21G, and HF/6-31G methods and pKa was found. The same linear relationship was found between the HOMO energies obtained by these methods and σ(p)(indicated p-position). Thus, the HOMO energy can be adopted instead of pKa and σ(p) for choosing the ylide as the donor in organic reactions. In addition, a linear relationship between the ν (C=O) stretching bands obtained by these methods and the parameters described above was found.

Hence, as for the electron donation of the ylide, it is noted that the HOMO energy can be used instead of pKa as a new method for showing the basicity of ylides. Furthermore, the ν(C=O) stretching bands obtained by these methods can be estimated by the HOMO energy obtained by the same methods.

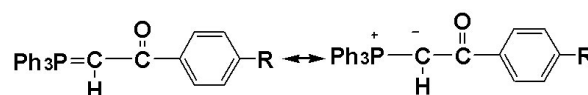**Keywords:** Ylides, HOMO energy, pKa, ν(C=O) stretching bands, Semi-empirical method, *ab initio* method

1   Introduction

An ylide can be defined as a substance in which a carbanion is attached directly to a heteroatom(X) carrying a high degree of positive charge - represented by the general formula **I**.

I

Ylides have two main canonical structures: $X^+ – Y^-$ and $X = Y$, whose relative contributions depend on the nature of the heteroatom and substituents. Phosphorus ylides employed in this study have a general structure often written as a hybrid.[**II**]

II

The structural requirement for a phosphorus ylide is that it contains an anionic carbon attached to a phosphorus atom which carries a high degree of positive charge. Thus, ylides have electronically unique characteristics because of the specific structures and are known to be electron donors[1–13].

The kinetics of the charge-transfer complex composed of TCNQ as the acceptor and phosphorus ylides (**ylides 1-3**) was reported. As the basicity on the ylide carbon (anionic carbon) of phosphorus ylides is controlled by substituents on ylide carbon, the correlation between pKa of the phosphorus ylide as the donor

and the formation of the phosphorus ylide-TCNQ charge-transfer complex was studied. The linear relationship between the reaction rate in the formation of charge-transfer complexes and pKa of the ylides was reported[13].

Although a vast number of basicity measurements in acetonitrile have been carried out, the reliability is still not good. Basicity data obtained by different authors often lack consistency and gaps exist[18]. And then, studies related to the pKa of the ylides[14–19] are still not sufficient.

Exact quantitative basicity data are very important in applying bases in various fields of chemistry and in designing new bases with desired properties. Thus, it is most necessary to discuss a new approach by the semi-empirical and *ab initio* methods for showing pKa of the ylides.
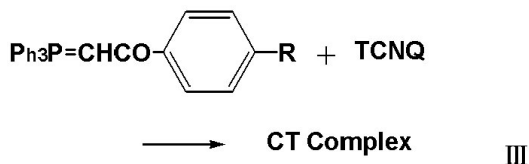
In this paper, it is reported that the HOMO energies obtained by the semi-empirical and *ab initio* methods[20–23], can be adopted instead of pKa as a new method for showing the basicity of ylides in organic reactions.

Since the $\nu(C=O)$ stretching bands are important as means to investigate the electronic structure of the ylide molecule[24, 25], those were calculated by the AM1, PM3, and MNDOD methods (by WinmopacVer3.0) and the HF/3-21G and 6-31G methods (by Spartan ' 04) in this study. These results were compared with the observed $\nu(C=O)$ stretching bands in ylide molecules. Furthermore, the relationships between the HOMO energy, pKa, the substituent constant $(\sigma(p))$[26], and the $\nu(C=O)$ stretching bands were also reported.

2   Results and discussion

2.1   The relationship between pKa and the HOMO energies in phosphorus ylides

The charge-transfer complexes were formed by the reaction of $Ph_3P=CH-C(=O)-C_6H_4-R(R=OMe(\textbf{ylide 1})$, R=H(**ylide 2**), and R=NO$_2$(**ylide 3**)) and TCNQ.[**III**]

We already found that there is a linear relationship between the rate constant, log k and pKa[13]. When the linear relationship is represented by the form log k = m(pKa) + c, the values of m and c are 0.43 and -1.77 at 50 °C, 0.43 and -1.87 at 40 °C, and 0.43 and -1.99 at 30 °C, respectively. This result indicates that the electron density of the donor molecule plays an important role in the formation of charge–transfer complexes. The substituent effect was also examined by the Hammett method[13]. In this case, the range of reaction constants (ρ) is from -1.06 to -1.17. The result shows that the rate constant increases when increasing the electron density at the reaction site.

In order to investigate the relationship between the HOMO energy and the degree of electron density in ylides, the HOMO energies in **ylides 1-3** were computed by three methods (AM1, PM3, and MNDOD), as shown in Table 1. The same calculations for $Ph_3P=CH-C(=O)-OMe(\textbf{ylide 4})$, $Ph_3P=C(Cl)-C(=O)-OMe(\textbf{ylide 5})$, and **ylides 6-9** were also carried out for comparison. These results are also shown in Table 1.

A linear relationship was not found between the HOMO energies obtained by the PM3 and MNDOD methods and pKa. The plot of the HOMO energy obtained by the AM1 method and pKa is shown in Figure 1 and a linear relationship was found. A linear relationship between the HOMO energy obtained by the AM1 method and $\sigma(p)$ was also found, as shown in Figure 2.

In addition, HOMO energies obtained by the HF/3-21G and 6-31G methods are shown in Table 1. Linear relationships were found between HOMO energies obtained by these methods, pKa, and $\sigma(p)$. The plots of HOMO energy obtained by the HF/6-31G method and both of pKa and $\sigma(p)$ are shown in Figures 3, 4, respectively. The HOMO energy agrees with the change of pKa caused by substituents.

The plot of the HOMO energy obtained by the AM1 method and the rate constant, log k at different temperatures is shown in Figure 5. In addition, a linear relation between the rate constant of the Wittig reaction, log k(Wittig) and the HOMO energy obtained by the same method was found, as shown in Figure 6. From these results, it is clarified that as there are close relationships between pKa, $\sigma(p)$, and HOMO energies obtained by the AM1, HF/3-21G, and HF/6-31G methods, thus HOMO energies can be used instead of pKa as a new method for considering the electron donation of **ylides 1-3** in organic reactions.

By comparing $Ph_3P=CH-C(=O)-C_6H_5$ (**ylide 2**) and $Ph_3P=C(Cl)-C(=O)-C_6H_5$ (**ylide 10**), the effect on electronic structure of introducing a Cl atom in ylides was investigated. The HOMO energy and pKa of **ylide 10** substituted by Cl atom is also shown in Table 1. The substitution of a Cl atom for hydrogen in **ylide 2** leads to higher HOMO energies in all methods. Thus, it is shown that the electron donation on carbon atom of **ylide 10** is increased by the Cl atom and its basicity is higher than that of **ylide 2**.

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Table 1. The HOMO energies (eV) in **ylides 1-10**, pKa, and substituent constant σ(*p*)

	ylide 1	ylide 2	ylide 3	ylide 4	ylide 5
Methods					
AM1	-8.367	-8.494	-8.924	-8.658	-8.560
PM3	-8.041	-8.079	-8.446	-8.214	-7.883
MNDOD	-8.150	-8.109	-8.458	-8.296	-7.888
pKa	6.7	6.0	4.2	8.8	
σ (*p*)	-0.268	0	0.778		

	ylide 6	ylide 7	ylide 8	ylide 9	ylide10
Methods					
AM1	-8.674	-8.743	-8.022	-8.442	-8.243
PM3	-8.026	-8.298	-8.037	-8.055	-7.763
MNDOD	-8.218	-8.319	-8.101	-8.113	-7.881
pKa					
σ (*p*)	0.502	0.660	-0.6	-0.320	

	ylide 1	ylide 2	ylide 3
Methods			
HF/3-21G	-7.59	-7.70	-8.14
HF/6-31G	-7.45	-7.60	-8.04
pKa	6.7	6.0	4.2
σ (*p*)	-0.268	0	0.778

$Ph_3P=CH-C(=O)-C_6H_4-R$
  R=OMe (**ylide 1**), R=H (**ylide 2**), R=NO$_2$ (**ylide 3**)
ylide 4 $Ph_3P=CH-C(=O)-OMe$
ylide 5 $Ph_3P=C(Cl)-C(=O)-OMe$
$Ph_3P=CH-C(=O)-C_6H_4-R$
  R=COMe (**ylide 6**), R=CN (**ylide 7**), R=NH$_2$ (**ylide 8**),
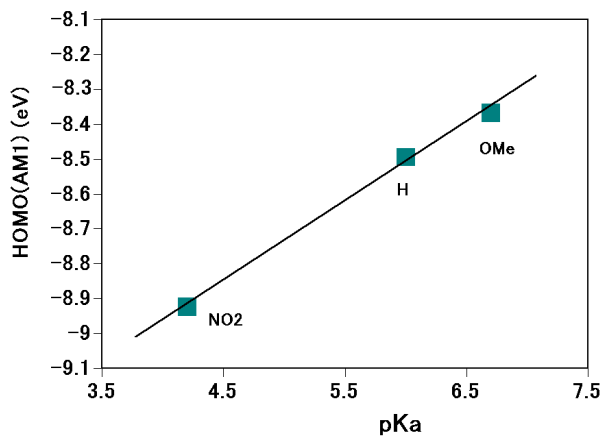 R=OH (**ylide 9**)
ylide 10 $Ph_3P=C(Cl)-C(=O)-C_6H_5$
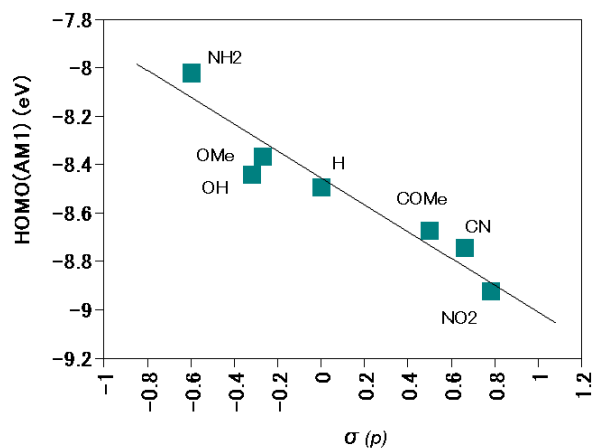

Figure 1. Relationship between HOMO(AM1) and pKa

Figure 2. Relationship between HOMO(AM1) and σ(*p*)

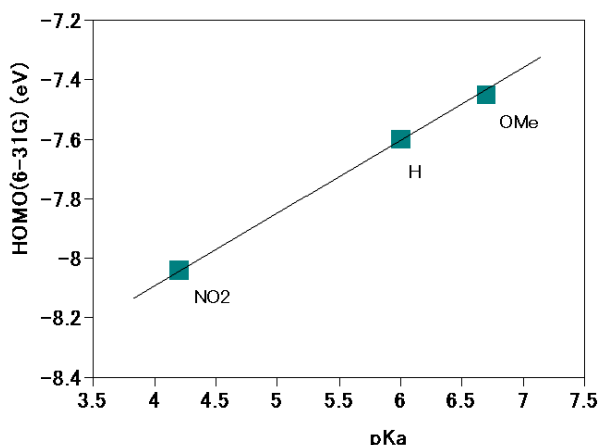Figure 3. Relationship between HOMO(6-31G) and pka

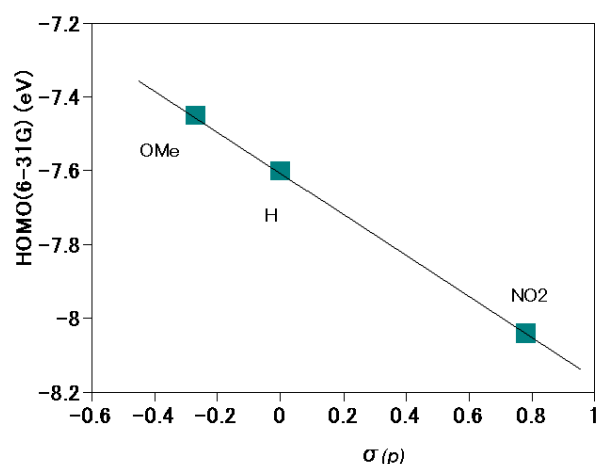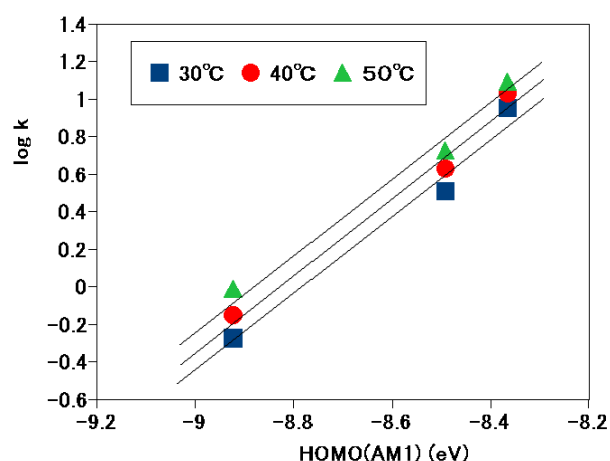Figure 6. Relationship between log k(Wittig) and HOMO(AM1)

Figure 4. Relationship between HOMO(6-31G) and $\sigma(p)$

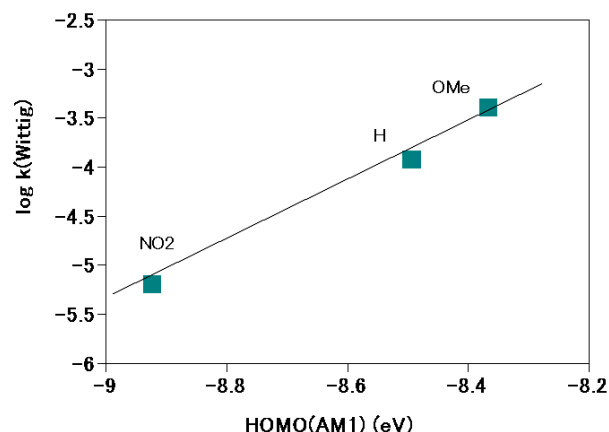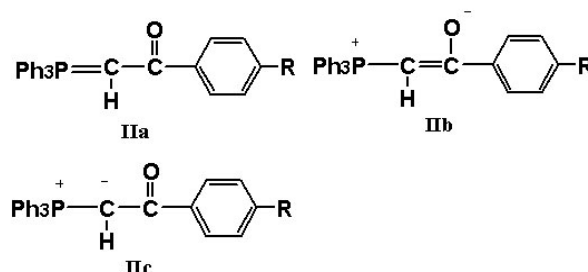Figure 5. Relationship between log k and HOMO(AM1) at different temperatures

2.2 Comparison of the ν(C=O) stretching bands in Ph_3P=CH-C(=O)-C_6H_4-R (R=OMe(ylide 1), R=H (ylide 2), R=NO_2 (ylide 3)) and corresponding phosphonium salts 11-13

Three resonance structures of Ph_3P=CH-C(=O)-C_6H_4-R[II] shown below have been presented [25]:

The ν(C=O) stretching bands in the corresponding salts shifted to higher frequency (135-189 cm^{-1}) in comparison with those of phosphorus ylides[25]. This result indicates that the contribution of resonance structure IIb is large in ylides. In addition, the ν(C=O) stretching bands of ylides in the charge-transfer complexes shifted to high frequency (30-60 cm^{-1})[13]. This shift shows the interaction with TCNQ and the ylide bond. Hence, it is noted that the ν(C=O) stretching band is a very important factor concerning the electronic structure of ylides.

The ν(C=O) stretching bands in **ylides 1-3** and corresponding phosphonium **salts 11-13** were computed by three methods (AM1, PM3, and MNDOD), and these results are shown in Table 2. The ν(C=O) stretching bands in phosphorus ylides shifted to lower frequency compared with those of phosphonium salts in all calculation methods.

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In addition, the ν(C=O) stretching bands in Ph$_3$P=CH-C(=O)-OMe(**ylide 4**) and Ph$_3$P=C(Cl)-C(=O)-OMe (**ylide 5**) were computed by three methods(AM1, PM3, and MNDOD) and these results are also shown in Table 2. The ν(C=O) stretching bands in phosphorus **ylides 4-5** were located at the middle of **ylides 1-3** and **salts 11-13** in both observed and calculated ν(C=O) stretching bands. Thus, it is shown that the degree of electron donation in **ylides 4-5** is less when compared with **ylides 1-3**. The differences between the ν(C=O) stretching bands in ylides and corrponding salts and means of those are shown in Table 3. The mean of these differences for observed ν(C=O) stretching bands was 144 cm^{-1}. Those for the ν(C=O) stretching bands obtained by the PM3 and MNDOD methods were 98, 93 cm^{-1}, respectively.

The differences between the ν(C=O) stretching bands obtained by the semi-empirical methods in ylides and corresponding salts were smaller than the observed result. It is suggested that the ν(C=O) stretching bands obtained by calculations can't reflect the unusual electronic structure of ylide molecules. In other words, the results obtained by the semi-empirical methods cannot give the correct change of polarity of the C=O group in ylide molecules.

2.3 Relationships between pKa, the substituent constant (σ (*p*)), the HOMO energy, and the ν(C=O) stretching band

The ν(C=O) stretching bands in simple carbonyl **compounds 14-15** and **amine imides 16-17** having the C=O group were investigated in order to compare with **ylides 1-3** and **4-5**[27, 28]. The ν(C=O) stretching bands in Ph-C(=O)-Me (**compound 14**), Ph-O-C(=O)-O-Me (**compound 15**), (p-NO$_2$-C$_6$H$_4$-CH$_2$)Me$_2$N$^+$-N$^-$C(=O)-CH$_3$ (**amine imide 16**), and (PhCH$_2$)Me$_2$N$^+$N$^-$C(=O)-Ph (**amine imide 17**) were calculated by the AM1, PM3, and MNDOD methods and these results are shown in Table 4.

The calculated ν(C=O) stretching bands in **amine imides 16-17** appeared at lower frequency by about 100 cm^{-1} than those of **compounds 14-15**, and the observed ν(C=O) stretching bands in **amine imides 16-17** showed a similar low frequency shift compared to those of **compound 14-15**. The PM3 method showed the smallest value for the mean of (calculated – observed) ν(C=O) stretching band. The ν(C=O) stretching bands in phosphorus **ylides 6-9** were computed by three methods (AM1, PM3, and MNDOD) and these results are shown in Table 5.

The ν(C=O) stretching band obtained by the MNDOD method did not change with σ(*p*). The plot of the ν(C=O) stretching band obtained by the PM3 method and σ(*p*) was divided into two groups and the good linear relationship was not found, as shown in Figure 7. The lin-

ear relationship between the ν(C=O) stretching band obtained by the AM1 method and pKa was found, as shown in Figure 8. The linear relationship between the ν(C=O) stretching band and σ(*p*) was also found, as shown in Figure 9. Then, the linear relationship between the ν(C=O) stretching band and the HOMO energy obtained by the AM1 method in **ylides 1-3** and **6-9** was found, as shown in Figure 10.

The AM1 method was the best for the estimation of ν(C=O) stretching bands in semi-empirical methods. The result obtained by the AM 1 method reflects clearly the change of the electronic structure of ylide molecules caused by the substitutent. The linear relationship between the observed ν(C=O) stretching band and the HOMO energy obtained by the AM1 method in phosphorus **ylides 1-3** was found, as shown in Figure 11.

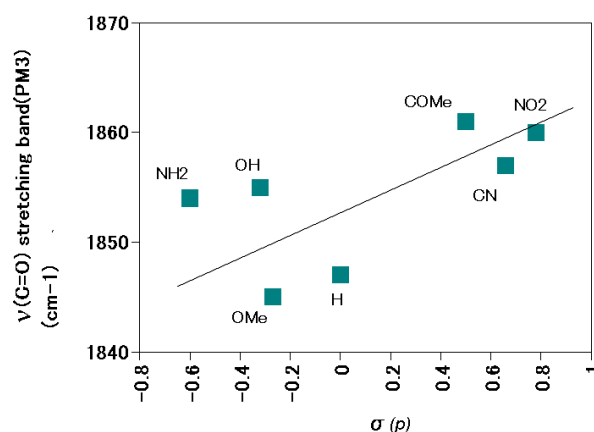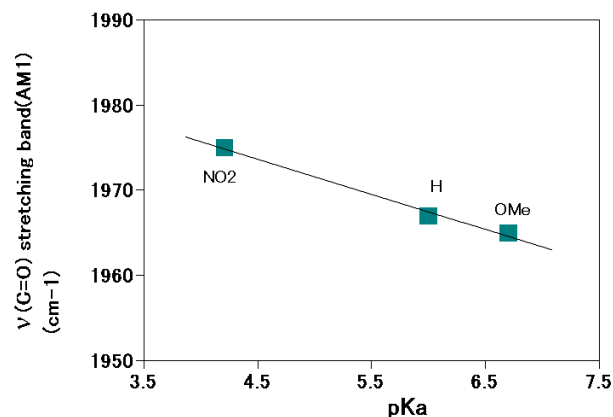Figure 7. Relationship between the ν(C=O) stretching band(PM3) and σ(*p*)

Figure 8. Relationship between the ν(C=O) stretching band(AM1) and pKa

Figure 9. Relationship between the ν(C=O) stretching band(AM1) and σ(p)

Figure 12. Relationship between the ν(C=O) stretching band(obs) and HOMO(6-31G)

Figure 10. Relationship between the ν(C=O) stretching band(AM1) and HOMO(AM1)

Figure 13. Relationship between the ν(C=O) stretching band(6-31G) and pKa

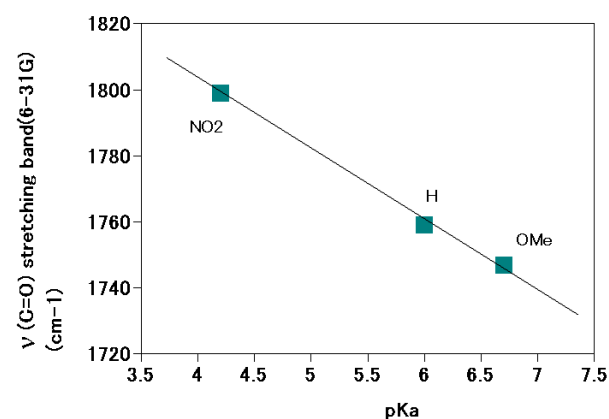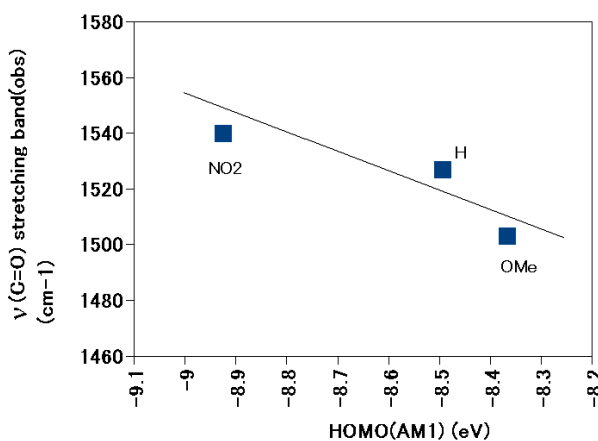
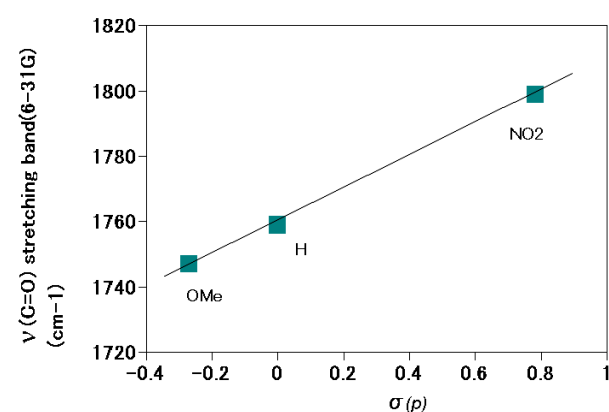Figure 11. Relationship between the ν(C=O) stretching band(obs) and HOMO(AM1)

Figure 14. Relationship between the ν(C=O) stretching band(6-31G)) and σ(p)

Table 2. The ν(C=O) stretching bands obtained by the AM1, PM3, and MNDOD methods, those observed, and the means of (calcd – obs) ν(C=O) stretching bands in **ylides 1-3**, phosphonium **salts 11-13**, and **ylides 4-5** (cm^{-1})

AM1 method Compounds	calculated ν(C=O) band	observed ν(C=O) band	mean of (calcd – obs) ν(C=O) band
ylide 1	1965	1503	
ylide 2	1967	1527	440
ylide 3	1975	1540	
phosphonium **salt 11**	2011	1652	
phosphonium **salt 12**	2027	1662	355
phosphonium **salt 13**	2029	1689	
ylide 4	2007	1621	386
ylide 5	2044	1642	

PM3 method Compounds	calculated ν(C=O) band	observed ν(C=O) band	mean of (calcd – obs) ν(C=O) band
ylide 1	1845	1503	
ylide 2	1847	1527	333
ylide 3	1860	1540	
phosphonium **salt 11**	1938	1652	
phosphonium **salt 12**	1953	1662	286
phosphonium **salt 13**	1956	1689	
ylide 4	1909	1621	276
ylide 5	1903	1642	

MNDOD method Compounds	calculatied ν(C=O) band	observed ν(C=O) band	mean of (calcd – obs) ν(C=O) band
ylide 1	2024	1503	
ylide 2	2025	1527	507
ylide 3	2025	1540	
phosphonium **salt 11**	2117	1652	
phosphonium **salt 12**	2117	1662	450
phosphonium **salt 13**	2118	1689	
ylide 4	2028	1621	394
ylide 5	2023	1642	

ylide 4 Ph$_3$P=CH-C(=O)-OMe, **ylide 5** Ph$_3$P=C (Cl)-C(=O)-OMe
Ph$_3$P$^+$-CH2-C(=O)-C$_6$H$_4$-R
  R=OMe (phosphonium **salt 11**), R=H (phosphonium **salt 12**),
  R=NO$_2$ (phosphonium **salt 13**)

The HOMO energies and the ν(C=O) stretching bands in **ylides 1-3** were also computed by the HF/3-21G and HF/6-31 methods in order to perform precise calculations. These results are shown in Tables 1 and 6, respectively. The ratios of observed band and those calculated using the HF/3-21G and 6-31G methods were 0.90-0.91 and 0.86-0.87, respectively.

The result obtained by the HF/6-31G method was found to be better than that obtained by the HF/3-21G method. Linear relationships between the observed ν(C=O) stretching bands and the HOMO energies obtained by the HF/3-21G and 6-31G methods in phosphorus **ylides 1-3** were found, and the result obtained by the HF/6-31G method is shown in Figure 12. Linear relationships were found between the ν(C=O) stretching bands and HOMO energies obtained by these methods, pKa, and σ(p). The plots of ν(C=O) stretching band and both of pKa and σ(p) are shown in Figures 13, 14, respectively. The plot of the ν(C=O) stretching band and HOMO energy is also shown in Figure 15.

Table 3. The differences between the calculated ν(C=O) stretching bands in ylides and corresponding salts, and means in the semi-empirical methods and Experiment (cm^{-1})

	AM1		Experiment	
Compounds	calculated $\Delta\nu$(C=O) band	(mean)	observed $\Delta\nu$(C=O) band	(mean)
The difference (**11**) - (**1**)	46		149	
The difference (**12**) - (**2**)	60	(53)	135	(144)
The difference (**13**) - (**3**)	54		149	

	PM3		MNDOD	
Compounds	calculated $\Delta\nu$(C=O) band	(mean)	calculated $\Delta\nu$(C=O) band	(mean)
The difference (**11**) - (**1**)	93		93	
The difference (**12**) - (**2**)	106	(98)	92	(93)
The difference (**13**) - (**3**)	96		93	

Table 4. The ν(C=O) stretching bands obtained by the AM1, PM3, and MN-DOD methods, those observed and the means of (calcd – obs) ν(C=O) stretching bands in carbonyl **compounds 14-15** and **amine imides 16-17** (cm^{-1})

AM1 method Compounds	calculated ν(C=O) band	observed ν(C=O) band	the mean of (calcd – obs) ν(C=O) band
compound 14	2038	1680	352
compound 15	2121	1775	
amine imide 16	1919	1580	337
amine imide 17	1904	1570	

PM3 method Compounds	calculated ν(C=O) band	observed ν(C=O) band	the mean of (calcd – obs) ν(C=O) band
compound 14	1955	1680	232
compound 15	1964	1775	
amine imide 16	1867	1580	292
amine imide 17	1859	1570	

MNDOD method Compounds	calculated ν(C=O) band	observed ν(C=O) band	the mean of (calcd – obs) ν(C=O) band
compound 14	2081	1680	372
compound 15	2117	1775	
amine imide 16	2038	1580	462
amine imide 17	2032	1570	

compound 14 Ph-C(=O)-Me, **compound 15** Ph-O-C(=O)-O-Me
amine imide 16 (p-NO$_2$-C$_6$H$_4$-CH$_2$)Me$_2$N$^+$N$^-$C(=O)-Me
amine imide 17 (PhCH$_2$)Me$_2$N$^+$N$^-$C(=O)-Ph

Since the ratio of the observed ν(C=O) stretching band and that calculated using the HF/6-31G method was 0.86 – 0.87, the ν(C=O) stretching band in ylides can be estimated from the HOMO energy obtained by this method and this ratio. Thus, the HOMO energy is useful to estimate the ν(C=O) stretching bands in ylides.

As a consequence, the ν(C=O) stretching bands obtained by the AM1, HF/3-21G, and HF/6-31G methods are closely related to σ (p), pKa, and the HOMO energy. Especially, it is clarified that the HOMO energy is an important parameter when considering the ν(C=O) stretching bands in ylides.

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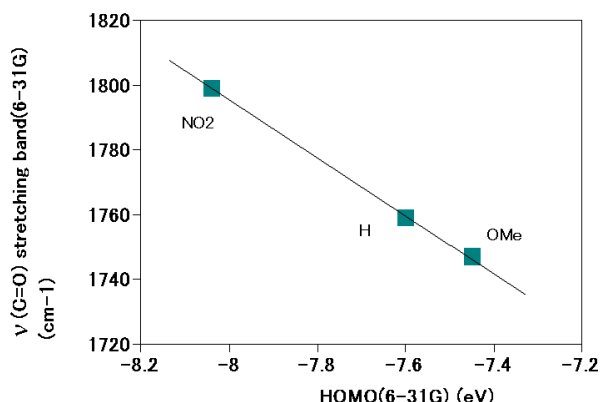*J. Comput. Chem. Jpn., Vol. 4, No. 2 (2005)*

Figure 15. Relationship between the ν(C=O) stretching band(6-31G) and HOMO(6-31G)

Table 5. The ν(C=O) stretching bands obtained by the AM1, PM3, and MNDOD methods in **ylides 6-9** (cm^{-1})

Methods	ylide 6	ylide 7	ylide 8	ylide 9
AM1	1975	1971	1962	1964
PM3	1861	1857	1854	1855
MNDOD	2024	2024	2024	2025
σ (*p*)	0.502	0.660	-0.6	-0.320

Ph$_3$P=CH-C(=O)-C$_6$H$_4$-R
    R=COMe (**ylide 6**), R=CN (**ylide 7**),
    R=NH$_2$ (**ylide 8**), R=OH (**ylide 9**)

Table 6. The ν(C=O) stretching bands obtained by the HF/3-21G and 6-31G methods (cm^{-1}) and the ratios of observed bands and those calculated in **ylides 1-3**

Methods	3-21G	6-31G		
Compounds	ν(C=O) band	ν(C=O) band	ratio of obs/calcd(3-21G)	ratio of obs/calcd(6-31G)
ylide 1	1658	1747	0.907	0.860
ylide 2	1689	1759	0.904	0.868
ylide 3	1694	1799	0.909	0.856

3   Conclusion

The electron donation of ylides is a very important factor in the formation of charge-transfer complexes and organic reactions. The basicity, pKa is already used as the parameter when choosing donors in the formation of charge-transfer complexes.

Data related to pKa of ylides are not enough. Especially, we pay attention to the HOMO energies obtained by the semi-empirical and *ab initio* methods instead of pKa. Linear relationships between pKa and the HOMO energies obtained by the AM1, HF/3-21G, and HF/6-31G methods were found. Linear relationships between the HOMO energies obtained by these methods and σ(*p*) were also found. It is clarified that the HOMO energies in ylides are useful to elucidate the change of pKa caused by substituents and can be used when choosing donors in various chemical reactions. Therefore, the semi-empirical and *ab initio* methods play a role in the determination of pKa of donors in organic reactions.

The ν (C=O) stretching bands in the charge-transfer complex are very important to investigate the interaction with TCNQ and the ylide carbon. Linear relationships between the ν(C=O) stretching bands and the HOMO energies obtained by the AM1, HF/3-21G, and HF/6-31G methods were found. The HF/6-31G method was found to be better than the HF/3-21G method in *ab initio* methods. Since the ratio of the observed ν(C=O) stretching band and that calculated using the HF/6-31G method was 0.86 – 0.87, the ν(C=O) stretching band in ylides can be estimated from the HOMO energy obtained by this method and this ratio. It is found from these results that the HOMO energy is useful to estimate the ν(C=O) stretching bands in ylides.

It is worthy of attention that close relations were found between pKa, σ(*p*), the ν(C=O) stretching band, and the HOMO energy in the ylide molecules.

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