

# Nature of 3d Orbitals in Ylides. Experimental and Theoretical Studies of the Ultraviolet Spectra of Cyclopentadienylides

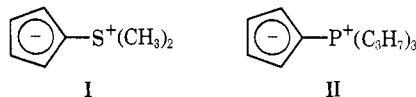
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**Abstract:** Two stable ylides, dimethylsulfonium cyclopentadienylide (I) and tri-*n*-propylphosphonium cyclopentadienylide (II), are synthesized, and their uv spectra are measured in several solvents. The spectrum measured in *n*-hexane consists of three bands, A, B, and C. When the solvent is changed from *n*-hexane to methanol, a large blue shift is observed on the longest wavelength band, A. A semiempirical MO calculation (the "method of composite molecule") for I and II has shown that the uv spectra of I and II can be satisfactorily explained by the 3d orbital of free sulfur or phosphorus (*i.e.*, by the Slater 3d orbital with effective nuclear charge  $Z_{3d} \approx 1.4$ ). The A band is assigned to the transition from the ground state of the ylide to that of the ylene (*i.e.*, an intramolecular electron-transfer-band), the B band to  $E_2'$  ( $D_{3h}$ ) of the cyclopentadienyl anion, and the C band to  $E_1'$  ( $D_{3h}$ ) of the cyclopentadienyl anion. The  $p\pi-d\pi$  resonance (ylide-ylene resonance) energies in the ground states are 32 kcal/mol for I and 31 kcal/mol for II, and the amounts of ylide structure in the ground state are 83% for I and 84% for II. The effect of molecular fields on 3d orbitals is also discussed.

Ylides have a highly polarized structure in which an anionic carbon is connected by a covalent bond to a sulfur or phosphorus atom bearing a positive charge. It is usually assumed that a negative charge on the anionic carbon is partly transferred into the 3d orbital of the sulfur or phosphorus cation, and thus the total energies of ylides are lowered.<sup>2</sup> Although many authors have discussed the  $p\pi-d\pi$  resonance in ylides,<sup>2</sup> there has so far been no theoretical study on their uv spectra.

In the present work two stable ylides, dimethylsulfonium cyclopentadienylide (I) and tri-*n*-propylphosphonium cyclopentadienylide (II), are prepared, and their uv spectra are measured in several solvents. As sulfonium and phosphonium ylides, I and II are chosen for the following reasons: (i) they are stable



enough to be purified for the measurement of their uv spectra and (ii) their spectra are simple enough to form a theoretical study. I is a recently reported compound<sup>3</sup> and II is newly synthesized in this work. In later sections, semiempirical calculations of the electronic structures of I and II are described and the nature of the 3d orbitals of sulfur and phosphorus is discussed.

## Experimental Section

**Preparation of I and II.** I was prepared according to the method of Behringer and Scheidl<sup>3</sup> and purified by sublimation at 80° under vacuum (0.002 mm), mp 129.5–130.0°.

Two parts of tri-*n*-propylphosphine<sup>4</sup> was added to one part of cyclopentene dibromide<sup>5</sup> in  $\text{CHCl}_3$ . After the mixture was allowed to stand for 1 week at room temperature, the precipitated phos-

phonium salt was extracted with water, and subsequent addition of a large amount of concentrated aqueous NaOH to the solution afforded II as a white powder (sometimes as an oil). II was recrystallized from *n*-hexane and sublimed at 60° under vacuum (0.01 mm); mp 67.8–69.5°; nmr, two multiplets between  $\tau$  3.65 and 3.73 (4 H) and 7.7 and 9.1 (21 H). *Anal.* Calcd for  $\text{C}_{14}\text{H}_{23}\text{P}$ : C, 74.96; H, 11.23. Found: C, 74.76; H, 11.14.

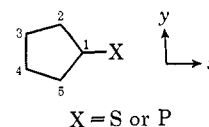
**Measurement of Uv Spectra.** Uv spectra of I and II were recorded on a Cary Model 15 spectrophotometer in *n*-hexane and in methanol under a dry nitrogen atmosphere between 185 and 400  $\mu$ . The spectra are shown in Figure 1. The oscillator strength ( $f$ ) was calculated by the usual method.

At first sight, the observed spectra seemed to be composed of two peaks, A (lower energy) and C (higher energy). However, by analyzing the spectra using a Du Pont 310 curve resolver, the third peak B was found between A and C. (The peaks were assumed to be Gaussian curves.) Although there was considerable uncertainty in resolving the spectra into A, B, and C, the energies of A and C could be determined within  $\pm 0.03$  and  $\pm 0.06$  eV, respectively, and the oscillator strengths of A and C within  $\pm 0.05$  and  $\pm 0.1$ , respectively. However, there was a large uncertainty in the energy and oscillator strength of B; in fact, we can only say that the energy of B is between 4.5 and 5.5 eV ( $f = 0.1-0.3$ ) for I and between 5 and 6 eV ( $f = 0.1-0.3$ ) for II (in *n*-hexane). The energies and oscillator strengths are summarized in Table I. The dotted lines in Figure 1 show typical examples of this resolution of the spectra.

When the solvent was changed from *n*-hexane to methanol, a large blue shift was observed in the A peak (0.35 eV for I and 0.25 eV for II) and a small red shift in the C peak of II (0.07 eV). The effect of solvents on the B peak could not be determined because of the large uncertainty in determining its energy.

## Method of Calculation

We consider six electrons in the  $\pi$  system composed of the five  $2p_z$  orbitals of carbons of the cyclopentadienyl ring and the  $3d_{zz}$  orbital of sulfur or phosphorus. The coordinate system and the number of each atom of cyclopentadienylide are determined as follows.



In the zeroth approximation, a cyclopentadienylide is considered to be a cyclopentadienyl anion substituted by a sulfonium or phosphonium cation. This highly

(1) (a) Institute for Chemical Research; (b) Department of Synthetic Chemistry.

(2) For example, see A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(3) H. Behringer and F. Scheidl, *Tetrahedron Lett.*, 1757 (1965).

(4) W. C. Dravies, P. L. Pearse, and W. J. Jones, *J. Chem. Soc.*, 1263 (1929).

(5) W. G. Young, H. K. Hall, Jr., and S. Winstein, *J. Amer. Chem. Soc.*, 78, 4338 (1956).

Table I. Uv Spectra of Cyclopentadienylides I and II

Compound	Transition	Theoretical Energy, eV			Band	Experimental Energy, eV		
		a <sup>a</sup>	b <sup>b</sup>	f <sup>c</sup>		In <i>n</i> -hexane	In methanol	f <sup>d</sup>
I	$\Psi_1' \rightarrow \Psi_1'$	5.72	4.19	0.09	A	4.19 ± 0.01	4.54 ± 0.02	0.2-0.3
	$\Psi_1' \rightarrow \Psi_{\pm 3}'$	5.98	6.16	0.02	B	4.5-5.5	5-6	0.1-0.2
	$\Psi_1' \rightarrow \Psi_{\pm 4}'$	7.54	7.72	1.18	C	6.36 ± 0.06	6.36 ± 0.05	1.2-1.0
II	$\Psi_1' \rightarrow \Psi_2'$	5.50	4.63	0.08	A	4.63 ± 0.02	4.88 ± 0.03	0.2-0.3
	$\Psi_1' \rightarrow \Psi_{\pm 3}'$	6.02	6.15	0.02	B	5-6	5-6	0.1-0.3
	$\Psi_1' \rightarrow \Psi_{\pm 4}'$	7.57	7.67	1.28	C	6.33 ± 0.06	6.26 ± 0.04	1.4-1.2

<sup>a</sup> Calculated for  $Z_{3d} = 1.40$ ,  $Q = 4.34$ ,  $E_1 = 6.5$  (D-J),  $E_2 = 4.9$  (D-J),  $E_0 = 3.68$  (experimental), and the other  $E$ 's given by L-M. <sup>b</sup> These values are determined so that the energy of  $\Psi_1' \rightarrow \Psi_2'$  just coincide with the observed energy of the A band measured in *n*-hexane, by treating  $\Delta (= Q + A - I_{3d})$  as an adjustable parameter and by leaving the other parameters as they are in (a). <sup>c</sup> Oscillator strengths are calculated by the usual method. <sup>d</sup> Measured in methanol.

polarized configuration is called "ylide." The non-polarized configuration in which one of the  $\pi$  electrons in the cyclopentadienyl anion is transferred into the 3d orbital of the substituent is called "ylene."<sup>2</sup> What is involved here is the calculation of the interaction

energies. Calculations for I and II can be performed by almost the same procedure which was used by Murrell<sup>8</sup> in his studies of monosubstituted benzenes. However, in our case, we must consider far more configurations than Murrell has done (*i.e.*, the ground and excited configurations of ylide and ylene; there is a total of 16 such configurations), because the difference between the ground-state energies of the ylide and ylene is small.

The  $\pi$ -electron systems of cyclopentadienyl anion and radical have been studied by Longuet-Higgins and McEwen (L-M)<sup>9</sup> by a semiempirical LCAO-MO method. That of the anion alone has been studied by Del Bene and Jaffé (D-J)<sup>10</sup> by the CNDO method. Their results are summarized in Table II. In the table,  $\phi_k$  ( $k = 0, \pm 1, \pm 2$ ) are the molecular orbitals of the cyclopentadienyl  $\pi$  system.<sup>9</sup> The five anionic wave functions,  $\Phi_1, \Phi_{\pm 2},$  and  $\Phi_{\pm 3}$ , represent in our case the five ylide wave functions,  $\Psi_1, \Psi_{\pm 2},$  and  $\Psi_{\pm 3}$ . The 11 ylene wave functions,  $\Psi_{\pm 4}, \dots, \Psi_{\pm 9}$ , are constructed from the 11 radical wave functions ( $\Phi_{\pm 4}, \dots, \Phi_{\pm 9}$ ) and the 3d<sub>z<sup>2</sup></sub> orbital ( $\chi$ ), as shown in Table III. The inclusion of the 3p<sub>z</sub> orbital into the calculation is considered to be unnecessary because a configuration in which the lone-pair electrons are promoted into 3d<sub>z<sup>2</sup></sub> and 3p<sub>z</sub> becomes vacant has a much higher energy (by  $\sim 20$  eV) than those for the configurations used in our calculations.

According to Murrell,<sup>8</sup> the energies of the ylene wave functions are given by<sup>11</sup>

$$E_k'(\text{ylene}) = E_k + \Delta_m$$

$$k = \pm 4, \pm 5, 6, \pm 7, \pm 8, \pm 9 \quad (1)$$

with

$$\Delta_m = Q_m + A - I_{3d}, \quad m = 0, \pm 1, \pm 2 \quad (2)$$

where the  $E_k$ 's are the energies of the cyclopentadienyl radical (in Table II),  $A$  is the electron affinity of the cyclopentadienyl radical,  $I_{3d}$  is the ionization potential of the 3d orbital, and  $Q_m$  is the electrostatic energy between the 3d orbital  $\chi$  and the molecular orbital  $\Phi_m$ . Table III shows which  $\Delta_m$  should be used for  $E_k'$  when  $E_k'$  is calculated by eq 1.

The ionization potentials of the 3d orbitals of sulfur and phosphorus are estimated from the atomic energy

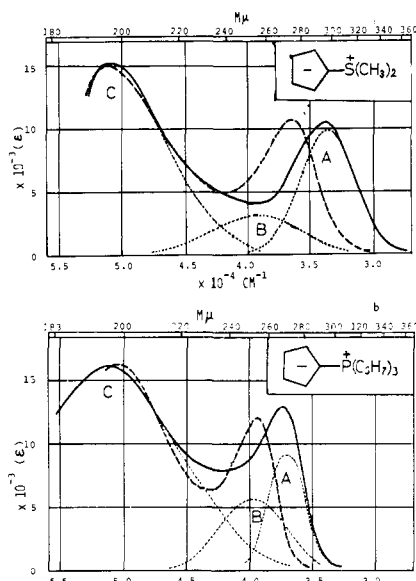


Figure 1. Uv spectra of cyclopentadienylides I and II: (a) dimethylsulfonium cyclopentadienylide (I), (b) tri-*n*-propylphosphonium cyclopentadienylide (II); (—) in *n*-hexane, (---) in methanol, (···) resolution of the spectrum in *n*-hexane into three peaks A, B, and C.

among the ground and excited configurations of the ylide and ylene. The method of solving this problem is known as the "method of composite molecule" or the "method of molecules in molecule," which was first proposed by Nagakura and Tanaka<sup>6</sup> and then given a theoretical foundation by Longuet-Higgins and Murrell.<sup>7,8</sup> The method of molecules in molecule is the most appropriate for our compounds for the following two reasons. First, it is easy to trace the physical meanings of each step of calculation and to find the wrong estimated parameters when the calculated values deviate from the observed ones. Secondly, this method gives much fruitful information such as the contributions of the ylide structure and the ylide-ylene reso-

(6) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

(7) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc., London, Sect. A*, **68**, 601 (1955).

(8) J. N. Murrell, *ibid., Sect. A*, **68**, 969 (1955).

(9) H. C. Longuet-Higgins and K. L. McEwen, *J. Chem. Phys.*, **26**, 719 (1957).

(10) J. Del Bene and H. H. Jaffé, *ibid.*, **48**, 4050 (1968).

(11) Note that the signs of the  $\Delta_m$ 's are contrary to those in Murrell's paper,<sup>8</sup> because in our case the ground state is the ionic (ylide) state.

**Table II.** Eigenfunctions and Energies of the Cyclopentadienyl Anion and Radical

Symmetry ( $D_{5h}$ )	Eigenfunction <sup>a</sup>	Energy, eV		
		L-M <sup>b</sup>	D-J <sup>c</sup>	Obsd <sup>d</sup>
Anion				
$^1A_1'$	$\Phi_1 =  0\bar{0}\bar{1}\bar{1}-1-\bar{1} $	$E_1 = 0$	0	
$^1E_1'$	$\Phi_{\pm 2} = (1/2) \left( \begin{array}{l}  0\bar{0}\bar{1}\bar{2}-1-\bar{1}  \pm  0\bar{0}\bar{1}\bar{1}-1-\bar{2}  \\ - 0\bar{0}\bar{1}\bar{2}-\bar{1}-\bar{1}  \mp  0\bar{0}\bar{1}\bar{1}-\bar{1}-\bar{2}  \end{array} \right)$	$E_2 = 7.22$	6.5	
$^1E_2'$	$\Phi_{\pm 3} = (1/2) \left( \begin{array}{l}  0\bar{0}\bar{1}\bar{2}-\bar{2}-1-\bar{1}  \pm  0\bar{0}\bar{1}\bar{1}-\bar{1}\bar{2}  \\ - 0\bar{0}\bar{1}\bar{2}-2-\bar{1}-\bar{1}  \mp  0\bar{0}\bar{1}\bar{1}-\bar{1}\bar{2}  \end{array} \right)$	$E_3 = 5.79$	4.9	
Radical				
$^2E_1''$	$\Phi_{\pm 4} =  0\bar{0}\pm 1\mp 1\mp 1 $	$E_4 = 0$		0
$^2E_1''$	$\Phi_{\pm 5} =  0\bar{0}\pm 1\pm \bar{1}\pm 2 $	$E_5 = 5.34$		
$^2A_2''$	$\Phi_6 =  \bar{0}\bar{1}\bar{1}-\bar{1}-1 $	$E_6 = 4.02$		3.65-3.71
$^2A_2''$	$\Phi_{\pm 7} = ( 0\bar{0}\bar{1}\bar{1}-2  \pm  0\bar{0}-1-\bar{1}\bar{2} )/\sqrt{2}$	$E_7 = 6.06$		
$^2A_1''$				
$^2E_2''$	$\Phi_{\pm 8} = [ 0\bar{0}\pm 1\mp \bar{1}\pm 2  -  0\bar{0}\pm 1\mp \bar{1}\pm 2 ]/\sqrt{2}$	$E_8 = 7.22$		
$^2E_2''$	$\Phi_{\pm 9} = 1/\sqrt{6} \left[ \begin{array}{l} 2 0\bar{0}\pm 1\mp \bar{1}\pm 2  -  0\bar{0}\pm 1\mp 1\pm 2  \\ - 0\bar{0}\pm 1\mp 1\pm 2  \end{array} \right]$	$E_9 = 5.79$		

<sup>a</sup>  $|0\bar{0}\bar{1}\bar{1}-1-\bar{1}|$ , for example, represents  $|\phi_0\bar{\phi}_0\phi_1\bar{\phi}_1\phi_{-1}\bar{\phi}_{-1}|$ . <sup>b</sup> Longuet-Higgins and McEwen.<sup>9</sup> <sup>c</sup> Del Bene and Jaffé.<sup>10</sup> <sup>d</sup> B. A. Thrush, *Nature (London)*, **178**, 155 (1956).

**Table III.** Wave Functions and Diagonal Elements of the Hamiltonian for Ylides I and II

Wave function <sup>a,b</sup>	Diagonal elements <sup>c</sup> of Hamiltonian
Ylide	
$\Psi_1 = \Phi_1$	0
$\Psi_{\pm 2} = \Phi_{\pm 2}$	$E_2$
$\Psi_{\pm 3} = \Phi_{\pm 3}$	$E_3$
Ylene	
$\Psi_{\pm 4} = (\Phi_{4\bar{\chi}} - \bar{\Phi}_{4\chi} \pm \Phi_{-4\bar{\chi}} \mp \bar{\Phi}_{-4\chi})/2$	$\Delta_{\pm 1}$
$\Psi_{\pm 5} = (\Phi_{5\bar{\chi}} - \bar{\Phi}_{5\chi} \pm \Phi_{-5\bar{\chi}} \mp \bar{\Phi}_{-5\chi})/2$	$E_5 + \Delta_{\pm 2}$
$\Psi_6 = (\Phi_{6\bar{\chi}} - \bar{\Phi}_{6\chi})/\sqrt{2}$	$E_6 + \Delta_0$
$\Psi_{\pm 7} = (\Phi_{\pm 7\bar{\chi}} - \bar{\Phi}_{\pm 7\chi})/\sqrt{2}$	$E_7 + \Delta_{\pm 2}$
$\Psi_{\pm 8} = (\Phi_{8\bar{\chi}} + \bar{\Phi}_{8\chi} \pm \Phi_{-8\bar{\chi}} \mp \bar{\Phi}_{-8\chi})/2$	$E_8 + \Delta_{\pm 2}$
$\Psi_{\pm 9} = (\Phi_{9\bar{\chi}} + \bar{\Phi}_{9\chi} \pm \Phi_{-9\bar{\chi}} \mp \bar{\Phi}_{-9\chi})/2$	$E_9 + \Delta_{\pm 2}$

<sup>a</sup>  $\Phi$ 's are the wave functions of cyclopentadienyl anion or radical. <sup>b</sup>  $\Phi_{6\bar{\chi}}$  or  $\bar{\Phi}_{6\chi}$ , for example, represents the Slater determinant  $\Phi_{6\bar{\chi}} = |\phi_0\bar{\phi}_0\phi_1\bar{\phi}_1\phi_{-1}\bar{\phi}_{-1}\bar{\chi}|$ ,  $\bar{\Phi}_{6\chi} = |\bar{\phi}_0\phi_0\bar{\phi}_1\phi_{-1}\bar{\phi}_{-1}\chi|$ . <sup>c</sup>  $E$ 's are given in Table II.  $\Delta$ 's are given by eq 2.

levels as follows

$$I_{3d}(S) = E(3s^23p^3; {}^4S_0) - (1/2)E(3s^23p^3({}^4S_0)3d; {}^5D) - (1/2)E(3s^23p^3({}^4S_0)3d; {}^3D) = 1.77 \text{ eV} \quad (3)$$

$$I_{3d}(P) = E(3s^23p^2; {}^3P_0) - (1/2)E(3s^23p^2({}^3P_0)3d; {}^4D) - (1/2)E(3s^23p^2({}^3P_0)3d; {}^2D) = 2.06 \text{ eV}$$

where the  $E$ 's are the energies of the electronic configurations indicated in the parentheses.<sup>12</sup>

The electron affinity  $A$  of the cyclopentadienyl radical is calculated by the  $\omega$  technique<sup>13</sup> and by the semiempirical method proposed by Hush and Pople.<sup>14</sup> Using the  $\omega$  technique, with  $\omega = 3.77$  or 3.73, which has been suggested by Scott and Becker,<sup>13</sup> we have found  $A = 1.64$  eV ( $\omega = 3.77$ ) and  $A = 1.74$  eV ( $\omega = 3.37$ ). By the semiempirical method we find  $A = 2.08$  eV, using the same C-C bond lengths as those in Hush and Pople's paper.<sup>14</sup> In the present work, we shall assume the intermediate value  $A = 1.89$  eV.

(12) C. E. Moore, *Nat. Bur. Stand. (U. S.), Circ.*, [1] No. 467, 163, 181 (1949).

(13) D. R. Scott and R. S. Becker, *J. Phys. Chem.*, **66**, 2713 (1962).

(14) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

The two-center repulsion integrals ( $rr|\chi\chi$ ) between  $\chi_r$  and  $\chi$ , which are required to calculate  $Q_m$ 's, are estimated theoretically using 2p and 3d Slater orbitals. According to the Slater rule, the effective nuclear charge  $Z_{3d}$  of the 3d orbital of free sulfur or phosphorus is equal to 1.00. However, Cruickshank, Webster, and Mayers,<sup>15</sup> having calculated the Hartree-Fock SCF 3d orbital of sulfur in  ${}^5D$ , have reported that this orbital is slightly more contracted than Slater's 3d orbital, and a suitable value of  $Z_{3d}$  is 1.39. In this work we assume  $Z_{3d} = 1.4$  both for sulfur and phosphorus and  $Z_{2p} = 3.25$  for carbon. According to the expression of Roothaan,<sup>16</sup> an electrostatic potential  $V$  at point  $(r, \theta, \phi)$  (in a spherical coordinate system) produced by a  $3d_{xz}$  orbital situated at the origin is given by

$$V(r, \theta, \phi) = [a|5S_b] + 2[a|5D\Sigma_b]P_2(\cos \theta) - 60[a|5G\Sigma_b]P_4(\cos \theta) + \{[a|5D\Sigma_b]P_{2,2}(\cos \theta) + 5[a|5G\Sigma_b]P_{4,2}(\cos \theta)\} \cos 2\phi \quad (4)$$

where the  $P$ 's are the Legendre polynomials.  $[a|5S_b] \dots [a|5G\Sigma_b]$  have been given by Kobayashi<sup>17</sup> as explicit functions of  $r$  and  $Z_{3d}$ . Since our 3d orbitals are spread widely in space, the 2p orbital of carbon can be approximated by two point charges of magnitude  $e/2$  separated by a distance  $d$ .<sup>18</sup> A number of  $Q_m$ 's are calculated with use of eq 4 for the parameters:  $1.6 \leq C_1-X \leq 1.9$  Å,  $1.2 \leq Z_{3d} \leq 1.6$ ,  $1.2 \leq d \leq 1.5$  Å, and  $m = 0, \pm 1, \pm 2$ , and it is found that the  $Q_m$ 's are almost independent of  $C_1-X$ ,  $d$ , and  $m$ , and depend only on  $Z_{3d}$ . In fact, the  $Q_m$ 's are given within  $\pm 0.07$  eV by

$$Q_m \approx 3.11Z_{3d} \text{ eV}, \quad m = 0, \pm 1, \pm 2 \quad (5)$$

It may be worth mentioning here that the two-center repulsion integrals calculated theoretically using Slater orbitals are usually too large because of neglect of the reorganization of  $\sigma$  electrons and inner-shell

(15) D. W. J. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, **40**, 3733 (1964).

(16) C. C. J. Roothaan, *ibid.*, **19**, 1445 (1951).

(17) H. Kobayashi, "Jikken Kagaku Koza," Vol. 11, S. Nagakura, Ed., Maruzen Co. Ltd., Tokyo, 1965, Chapter 4.

(18) The distance  $d$  is determined, for example, by the centers of the equivalent charged-sphere model proposed by Pariser and Parr,<sup>19</sup> *i.e.*,  $d = 4.597/Z_{2p} = 1.41$  Å.

(19) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

electrons; this effect was first pointed out by Pariser and Parr.<sup>19</sup> In fact, as is shown later, we must assume very small  $Q$  values to fit the calculated energies with the observed ones.

Substitution of these  $I_{3d}$ ,  $A$ , and  $Q$  values into eq 2 leads to  $\Delta(\text{sulfur}) = 4.46$  eV and  $\Delta(\text{phosphorus}) = 4.17$  eV; this result indicates that the ground states of I and II are  $\Psi_1(\text{ylide})$ . In what follows, however,  $\Delta$  will be allowed to change considerably around 4.46 or = 4.17 eV. The change of  $\Delta$  value is of course attributed mainly to a change in  $Q$  values.

The off-diagonal elements of the total electronic Hamiltonian are calculated in the same manner as was done by Murrell<sup>18</sup> and are summarized in Table IV.

Table IV. Off-Diagonal Elements of the Hamiltonian<sup>a</sup>

$$\begin{aligned}\beta_0' &= H_{1,6}/\sqrt{2} (= 2.12 \text{ eV for I and } 2.11 \text{ eV for II}) \\ \beta_1' &= H_{1,4}/\sqrt{2} = \sqrt{2}H_{\pm 3, \pm 5} = \sqrt{2}H_{\pm 2, \pm 7} = \sqrt{3}H_{\pm 2, \pm 9} = \\ & 2\sqrt{3}H_{\pm 3, \pm 9} (= 0.68 \text{ eV for I and } 0.72 \text{ eV for II}) \\ \beta_2' &= \sqrt{2}H_{\pm 2, \pm 4} = \sqrt{2}H_{\pm 3, \pm 4} (= 0.10 \text{ eV for I and II}) \\ \beta_k' &= (1 - (1/2)\delta_{0k})^{1/2} \sum_{r=1}^5 \cos [2k(r-1)\pi/5] \beta_{rX}\end{aligned}$$

<sup>a</sup>  $\beta_{rX}$  is the resonance integral between  $\chi_r$  and  $\chi_X$ .

The resonance integrals are calculated by the following approximation

$$\beta_{rX} = S_{rX}(I_{2p} + I_{3d})/2 \quad (6)$$

where  $S_{rX}$  is the overlap integral between  $\chi$  and  $\chi_r$  and  $I_{2p}$  is the ionization potential of the 2p orbital of carbon ( $I_{2p} = 11.42$  eV). The overlap integrals are found in Jaffé's table.<sup>20</sup> Though the 3d orbital under consideration is quite diffuse, the overlap integral between  $\chi$  and  $\phi_0$  is unexpectedly large because  $\phi_0$  itself is spread homogeneously over the cyclopentadienyl ring; with  $Z_{3d} = 1.4$ , this overlap integral amounts to 0.321 for I and 0.314 for II. The off-diagonal element  $H_{1,6}$  between  $\Psi_1$  and  $\Psi_6$  amounts, therefore, to 2.99 eV for both I and II. Other off-diagonal elements are all less than or equal to 1 eV. Numerical values of  $\beta_k'$  for  $Z_{3d} = 1.4$  are shown in Table IV. Since  $\beta_2'$  is very small (0.1 eV), we neglect it in later calculations.

## Results and Discussion

A number of secular determinants were solved numerically by a FACOM 230-60 computer at the Data Processing Center, Kyoto University.<sup>21</sup> Typical examples of the results are shown in Tables I (energies and oscillator strengths) and V (eigenfunctions). From these results it is concluded that the A band may be assigned to  $\Psi_1' \rightarrow \Psi_2''$ , the B band to the combination of  $\Psi_1' \rightarrow \Psi_{\pm 3}'$ , and the C band to the combination of  $\Psi_1' \rightarrow \Psi_{\pm 4}'$ . Energies in column a in Table I are calculated for  $Z_{3d} = 1.40$ ,  $Q = 4.36$ ,  $E_1 = 6.5$  (D-J),  $E_2 = 4.9$  (D-J),  $E_6 = 3.68$  (experimental), and the other  $E$ 's given by L-M. The energies in column b are determined so that the calculated energy of  $\Psi_1' \rightarrow \Psi_2'$  is just coincide with the observed energy of the A band measured in *n*-hexane, by treating  $\Delta (= Q + A - I_{3d})$  as an adjustable parameter and by fixing the other parameters to the above-mentioned values.

(20) H. H. Jaffé, *J. Chem. Phys.*, **21**, 258 (1953).

(21) The program used in the calculation was written by H. Sugimoto.

Table V. Eigenfunctions of Tri-*n*-propylphosphonium Cyclopentadienylyde (II)<sup>a</sup>

Eigenfunction	Energy, eV	% ylide
$\Psi_1' = 0.918\Psi_1 - 0.208\Psi_4 - 0.337\Psi_6$	-1.33	84.3
$\Psi_{-2}' = 1.000\Psi_4$	3.13	0.0
$\Psi_2' = 0.168\Psi_1 + 0.975\Psi_4 - 0.144\Psi_6$	3.30	2.8
$\Psi_{\pm 3}' = 0.013\Psi_{\pm 2} + 0.989\Psi_{\pm 3} - 0.138\Psi_{\pm 5} - 0.002\Psi_{\pm 7} - 0.052\Psi_{\pm 9}$	4.82	97.8
$\Psi_{\pm 4}' = 0.972\Psi_{\pm 2} - 0.021\Psi_{\pm 3} + 0.005\Psi_{\pm 5} - 0.174\Psi_{\pm 7} - 0.153\Psi_{\pm 9}$	6.34	94.5
$\Psi_5' = 0.358\Psi_1 + 0.075\Psi_4 + 0.930\Psi_6$	7.96	12.8
$\Psi_{\pm 6}' = -0.011\Psi_{\pm 2} + 0.135\Psi_{\pm 3} + 0.989\Psi_{\pm 5} + 0.008\Psi_{\pm 7} - 0.063\Psi_{\pm 9}$	8.54	1.8
$\Psi_{\pm 7}' = 0.106\Psi_{\pm 2} + 0.056\Psi_{\pm 3} + 0.056\Psi_{\pm 5} - 0.255\Psi_{\pm 7} + 0.958\Psi_{\pm 9}$	8.98	1.4
$\Psi_{\pm 8}' = 0.207\Psi_{\pm 2} + 0.012\Psi_{\pm 3} + 0.007\Psi_{\pm 5} + 0.951\Psi_{\pm 7} + 0.229\Psi_{\pm 9}$	9.30	4.3
$\Psi_9' = 1.000\Psi_8$	10.35	0.0

<sup>a</sup> Calculated for the same parameters as (b) in Table I. The eigenfunctions of I are almost the same as these.

The last column of Table V shows the percentage of ylide (% y) for each eigenfunction. The ground-state  $\Psi_1'$  is almost ylide (% y = 83-84), while  $\Psi_2'$  is almost pure ylene (% y = 3). Then,  $\Psi_1' \rightarrow \Psi_2'$  is a transition from a highly polarized state to a nonpolarized state; for such a transition (which is usually called an "intramolecular electron-transfer-band") a large blue shift is expected when the solvent is changed from nonpolar to polar. Large blue shifts are in fact observed for the A band (0.35 eV for I and 0.25 eV for II)<sup>22</sup> when the solvent is changed from *n*-hexane to methanol. Though the calculated energies of  $\Psi_1' \rightarrow \Psi_2'$  in column a in Table I are considerably larger than the observed energies of the A bands, we are sure from this solvent effect that the A band is assigned to  $\Psi_1' \rightarrow \Psi_2'$ . Since the energy of  $\Psi_1' \rightarrow \Psi_2'$  depends most strongly on  $\Delta (= Q + A - I_{3d})$ , the disagreement between the calculated and the observed energy must be attributed to the inaccuracy in the estimation of  $\Delta$  following eq 2, 3, and 5 and  $A = 1.89$  eV. If the original values,  $\Delta = 4.46$  eV for I or  $\Delta = 4.17$  eV for II, are depressed to 2.62 (I) or to 3.12 eV (II), the energy of  $\Psi_1' \rightarrow \Psi_2'$  becomes just equal to that of the A peak (column b in Table I). If these changes of  $\Delta$  values are, as is suggested in the previous section, all attributed to the depression of  $Q$  values calculated theoretically by eq 5, the original value  $Q = 4.34$  eV must be depressed to 2.50 eV for I and to 3.29 eV for II. These magnitudes of depression of  $Q$  values are not unreasonable (though they are somewhat too large), compared with those of the two-center repulsion integrals proposed by Pariser and Parr<sup>19</sup> for the carbon 2p orbital.<sup>23</sup>

The transitions  $\Psi_1' \rightarrow \Psi_{\pm 3}'$  are composed almost entirely of the local excitations  $\Phi_1 \rightarrow \Phi_{\pm 3}$  [ $E_2'$  ( $D_{5h}$ )] in the cyclopentadienyl anion and  $\Psi_1' \rightarrow \Psi_{\pm 4}'$  almost entirely of the other local excitations  $\Phi_1 \rightarrow \Phi_{\pm 2}$  [ $E_1'$  ( $D_{5h}$ )] in the cyclopentadienide anion (see Tables III and V); these transitions can be called "local excitation bands." If D-J's values (Table II) are used for  $E_1$

(22) The blue shift of II is smaller than that of I. A possible explanation of this observation is that the substituent groups of the phosphorus atom in II (*i.e.*, *n*-C<sub>3</sub>H<sub>7</sub>) are so bulky that polar solvent molecules cannot effectively interact with the charges on II.

(23) In the Pariser-Parr approximation, the two-center repulsion integral for ethylene (C-C = 1.34 Å) is depressed from 9.26 (estimated nonempirically) to 7.38 eV.

and  $E_2$ , the energies of  $\Psi_1' \rightarrow \Psi_{\pm 3}'$  become closer to the observed energies of the B bands and the energies of  $\Psi_1' \rightarrow \Psi_{\pm 4}'$  nearer to the observed energies of C bands than if L-M's values (in Table II) are used for  $E_1$  and  $E_2$ . Therefore, we conclude that D-J's values are closer to the exact values than L-M's. Since the polarity of the molecule is not changed strongly during these local excitations, the transition energies are expected to be affected only slightly by the polarity of the solvent (as was confirmed in our experiments).<sup>24</sup>

We conclude that the uv spectra of cyclopentadienylides I and II are explained by the 3d orbitals of a free sulfur or phosphorus.

The ylide-ylyene resonance energies in the ground state [*i.e.*,  $E(\Psi_1) - E(\Psi_1')$ ] are 1.40 eV (32 kcal/mol) for I and 1.33 eV (31 kcal/mol) for II. The amounts of ylide in the ground states are 83% for I and 84% for II. These values are different from those (% y = 50)<sup>25</sup> proposed by Ramirez, *et al.*, based on dipole moment measurements.

Our conclusion above seemingly contradicts the molecular field theories,<sup>26</sup> which have shown that 3d orbitals in most compounds are, compared with free 3d's, strongly contracted, and their energies are largely lowered by the molecular field produced by even weakly electronegative elements such as carbon.<sup>27</sup> We wish to answer this question and to show that our results are not a contradiction.

Let R be cyclopentadienyl fragment and X the substituted heteroatom, respectively. The total electronic Hamiltonian is given by

$$H(1, 2) = \sum_{i=1}^2 [K(i) - V_R(i) - V_X(i)] + \frac{1}{r_{12}} + H_R^0 + H_X^0 \quad (7)$$

where, for simplicity, two  $\pi$  electrons rather than six are considered explicitly;  $K(i)$  is the kinetic term,  $V_R(i)$  is the interaction among the  $i$ th electron and all the electrons and all the atomic charges in R,  $V_X(i)$  is the similar term for X,  $r_{12}$  is the repulsion between electrons 1 and 2, and  $H_R^0$  and  $H_X^0$  are the Hamiltonians for the inner electrons of R and X, respectively. Further, the Hamiltonians  $H_{R^{\cdot}}(1, 2)$ ,  $H_{R^{\cdot}}(1)$ , and  $H_{X^{\cdot}}(2)$  are given by

$$\begin{aligned} H_{R^{\cdot}}(1, 2) &= \sum_{i=1}^2 [K(i) - V_R(i)] + \frac{1}{r_{12}} + H_R^0 \\ H_{R^{\cdot}}(1) &= K(1) - V_R(1) + H_R^0 \\ H_{X^{\cdot}}(2) &= K(2) - V_X(2) + H_X^0 \end{aligned} \quad (8)$$

where  $H_{R^-}$  and  $H_{R^{\cdot}}$  are the Hamiltonians for the cyclopentadienide anion ( $R^-$ ) and radical ( $R^{\cdot}$ ), and  $H_{X^{\cdot}}$  is the Hamiltonian for neutral  $X^{\cdot}$ , respectively. If  $\phi$  is the highest occupied SCF-MO of radical  $R^{\cdot}$  and  $\chi$  is that of  $X^{\cdot}$  (in our case  $\chi$  is the 3d orbital of a free and neutral S or P), the electron affinity of  $R^{\cdot}$  and the

(24) A small red shift is observed on the C band of II; but, since the direction of the shift is contrary to that of the A band, it does not contradict our explanation. The effect of solvents on the B band is unknown.

(25) F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, **79**, 67 (1957).

(26) We wish to acknowledge a referee who pointed out the importance of the molecular field theory in treatment of 3d orbitals.

(27) D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601, 609 (1962); see also K. A. R. Mitchell, *J. Chem. Soc. A*, 2683 (1968); *Chem. Rev.*, **69**, 157 (1969).

ionization potential of  $X^{\cdot}$  may be given by

$$\begin{aligned} A_R &= \langle \phi | H_R | \phi \rangle - \langle \phi | \bar{\phi} | H_R | \phi \bar{\phi} \rangle \\ I_X &= \langle \chi | H_X | \chi \rangle \end{aligned} \quad (9)$$

Since in this model the ylide state is  $\Psi_1 = |\phi \bar{\phi}|$  and the ylyene state is  $\Psi_2 = |\phi \bar{\chi}|$ , we have

$$\begin{aligned} E(\text{ylene}) &\equiv H_{22} - H_{11} = \\ A_R - I_X + Q &+ \langle \phi | V_X | \phi \rangle - \langle \chi | V_R | \chi \rangle \end{aligned} \quad (10)$$

$$Q \equiv \iint \phi(1)\chi(2) \frac{1}{r_{12}} \phi(1)\chi(2) dr_1 dr_2 \quad (11)$$

Usually the last two terms in (10) are neglected and we find the equation (1) for the ground state of ylyene (*i.e.*,  $E_X = 0$ ). Of course, when the six  $\pi$  electrons are considered explicitly, the formulation becomes somewhat more complicated than those described above, but the point is quite the same.

Now the problem treated by Craig and Zauli may be presented for our model as follows

$$\begin{aligned} H_{X^{\cdot}}^{\text{mf}}(2) &= K(2) - V_X(2) + H_X^0 + \\ &\left\{ -V_R(2) + \int \phi(1) \frac{1}{r_{12}} \phi(1) dr_1 \right\} \end{aligned} \quad (12)$$

where the term in braces represents the molecular field of radical  $R^{\cdot}$  and Craig and Zauli's 3d (we denote it  $\chi^{\text{mf}}$ ) is the SCF function  $H_{X^{\cdot}}^{\text{mf}}$  in which the molecular field is kept constant. The ionization potential of  $\chi^{\text{mf}}$  is defined by

$$I_X^{\text{mf}} = \langle \chi^{\text{mf}} | H_{X^{\cdot}}^{\text{mf}} | \chi^{\text{mf}} \rangle \quad (13)$$

and we find

$$E(\text{ylene}) = A_R - I_X^{\text{mf}} + \langle \phi | V_X | \phi \rangle \quad (14)$$

in which the last term can be again neglected. Equation 14 is different from (10) and it is evidently not  $\chi^{\text{mf}}$  but  $\chi$  (*i.e.*, the free 3d orbital) that is to be used in our calculation. If  $Q$  is omitted and the  $I_{3d}$  is replaced by  $I_{3d}^{\text{mf}}$  in eq 3, we will have a new composite molecule method in regard to  $\chi^{\text{mf}}$  which is, generally speaking, expected to be more accurate than the old one. In other words, the inclusion of the molecular field leads to a better approximation.<sup>28</sup> There remains another question. Although the 3d orbital in our calculation is free from the molecular field of  $R^{\cdot}$ , it is still affected by fields produced by the substituents ( $\text{CH}_3$  or  $n\text{-C}_3\text{H}_7$ ), which are, according to Craig and Zauli, expected to be as important as that produced by  $R^{\cdot}$ .<sup>29</sup> However, if this is so, the fields made by the surrounding solvent molecules must also be important, and the summation of the former and the latter fields will give a rather homogeneous field over all space, so that  $\chi$  is affected only slightly by the summed fields. We may then conclude that it is only a poor improvement of the theory to include the fields which do not participate directly in the ylide bonding.

In summary, the apparent disagreement between our conclusion and that of the molecular field theory is

(28) However, from a practical point of view, one cannot expect that the new method will always predict the spectrum more accurately than the old one, because in the former  $I_{3d}^{\text{mf}}$  is calculated nonempirically, while in the latter  $I_{3d}$  is given empirically by (3).

(29) Note that the fields produced by  $\text{CH}_3$  or  $n\text{-C}_3\text{H}_7$  groups are included in  $H_X^0$ .

not a contradiction, but only a reflection of the difference between the approximations employed; it is not surprising that the valence orbitals of atoms in compounds will become largely different from those of free atoms when, as has been done by Craig and Zauli, a higher approximation is taken. The problem is whether the higher approximation is necessary or not in order to interpret electronic structures of molecules. It is, therefore, a happy finding for those who desire matters to be as simple as possible that our

ylides I and II can be adequately treated by the ordinary procedure using the free 3d orbitals of the sulfur of phosphorus atom, which predicts their energies semi-quantitatively.

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## A Generalized Orbital Description of the Reactions of Small Molecules<sup>1</sup>

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**Abstract:** The usual Hartree-Fock method leads to an improper description of the breaking of a bond, a problem that is overcome by the generalized valence-bond method. This method uses one orbital per electron as in the valence-bond method, but solves for the orbitals self-consistently as in the Hartree-Fock method. In this paper we consider the changes in the orbitals as the H<sub>2</sub> and LiH bonds are broken and we consider the orbital description of the H<sub>2</sub> + D ⇌ H + HD and LiH + H ⇌ Li + H<sub>2</sub> exchange reactions. We find that this orbital description leads to simple concepts in terms of which the changes in the system during reaction can be understood. It is expected that these concepts will apply to a large number of reactions.

A primary goal of chemistry is to elucidate the details of the processes occurring during chemical reactions. Thus, one wants to understand how all the bonds distort, form, and break in the transition region and why some reactions have high activation energies while others have low ones. Unfortunately, the intermediate states in such reactions are quite ephemeral, leading to difficulties in experimentally establishing an unambiguous description of the states in the transition region. Theoretical studies of such states, however, can be quite informative, since we can choose the nuclear configuration and reaction path and can examine in detail the changes in the bonding for each likely course of the reaction. Even so, not every theoretical approach is equally useful. It is not only necessary that the theoretical method lead to an accurate description of the potential surface or interaction energy, but it is also important that the resulting wave functions lead to concepts useful in understanding the relationships between whole classes of reactions.

The most generally used theoretical approach for *a priori* calculations of the wave functions of molecules has been the Hartree-Fock method or approximations thereto. Despite many successes in describing the ground states of molecules, this method has a key deficiency in its inability to describe properly the processes of breaking a bond.<sup>4</sup> We have found that an alterna-

tive approach, the generalized valence-bond (GVB) method, leads to a proper description of bond breaking and yet retains the useful orbital interpretation. This method has been far less extensively developed than the Hartree-Fock method; however, calculations on some simple reactions have now been carried out and lead to some concepts that are expected to be of rather general applicability.

We will concentrate here on the description of the H<sub>2</sub> + D ⇌ H + HD and LiH + H ⇌ Li + H<sub>2</sub> exchange reactions with an emphasis on the orbital description of these systems in the transition region.

### The Theoretical Methods for the Calculation of Molecular Wave Functions

First, some comparison between the Hartree-Fock and GVB methods will be appropriate.

**The Hartree-Fock Method.** A common approach for electronic wave functions of molecules has been the Hartree-Fock method,<sup>5</sup> in which the wave function is taken as an antisymmetrized product (determinant) of spatial and spin functions; the antisymmetrization ensures that Pauli's principle is satisfied. Thus, for H<sub>2</sub> the Hartree-Fock wave function is

$$\mathfrak{A}[\phi(1)\alpha(1)\phi(2)\beta(2)] = \phi(1)\phi(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (1)$$

where  $\mathfrak{A}$  is the antisymmetrizer (determinant operator),  $\phi$  is the best possible doubly occupied spatial orbital,

(5) D. R. Hartree, "The Calculation of Atomic Structures," Wiley, New York, N. Y., 1957.

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(4) E.g., R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).