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The Electronic Structures of Unstable Intermediates. Benzyne and Hetarynes

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A semi-empirical SCF MO method for valence electron systems, a modification of our previous method made by introducing the zero-differential overlap approximation except for the one-center exchange integrals, is presented. The results calculated for benzene, pyridine, pyrimidine and thiophene, the parent molecules of benzyne and hetarynes, using this modified method are compared with those obtained by the other calculations and experiments. The unstable intermediates treated in the present paper are benzyne, pyridynes, pyrimidyne and thiophynes. The unknown bond lengths of benzyne and hetarynes are estimated by a semi-empirical relation given in the present treatment. The nature of the carbon-carbon triplet bonds of benzyne and hetarynes is studied on the basis of the bond lengths and the total π bond orders for these bonds. The charge distributions and excitation energies of benzyne and hetarynes, and the chemical reactivity of some hetarynes are also discussed. The lowest triplet states of these intermediates are shown to be close to the singlet ground states.

In our previous series of papers[1-5] a semi-empirical SCF MO treatment for all valence electron systems was presented; this treatment has been shown to be useful in elucidating the electronic structures of various molecules. In the present paper the zero-differential overlap approximation, except for the one-center exchange integrals, is introduced into our previous method[1-5] in order to simplify its procedure and at the same time to make it applicable to large molecular systems.*1 Using this modified method, the electronic structures of benzyne and hetarynes are calculated, and the interatomic distances of these unstable intermediates estimated by a semi-empirical relation. The character of the triple bonds and the ground states of benzyne and hetarynes are discussed.[6]

Theoretical

The molecular orbital (MO) is taken as a linear combination of all the valence atomic orbitals (AO's) centered on the atoms of a molecule. Introducing the zero-differential overlap approximation, except for the one-center exchange integrals, the diagonal elements of the Fock's operator for a closed-shell molecule are given by:

$$F_{rr} = H_{rr} + \frac{1}{2}P_{rr}(rr|rr) + \sum_{r'(\neq r)}^{\text{on A}} P_{r'r'}\left[(rr|r'r') - \frac{1}{2}(rr'|rr')\right] + \sum_{\text{B}(\neq\text{A})} \sum_{s}^{\text{on B}} P_{ss}(rr|ss)$$

(r belonging hereafter to the A atom) (1)

1) T. Yonezawa, K. Yamaguchi and H. Kato, This Bulletin, **40**, 536 (1967).

2) T. Yonezawa, H. Nakatsuji and H. Kato, *ibid.*, **39**, 2788 (1966).

3) T. Yonezawa, H. Konishi and H. Kato, *ibid.*, **40**, 1071 (1967).

4) H. Kato, H. Konishi and T. Yonezawa, *ibid.*, **40**, 1017 (1967).

5) H. Kato, H. Konishi, H. Yamabe and T. Yonezawa, *ibid.*, **40**, 2761 (1967).

*1 The present method differs in the parametrizations of the diagonal and off-diagonal core integrals and one and two-center repulsion integrals from the CNDO method of Pople *et al.* (Ref. 17). Recently, Bene and Jaffé treated benzene, pyridine, and diazines by means of a modified CNDO method (J. D. Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968)).

6) Some of these results were reported in a preliminary communication: T. Yonezawa, H. Konishi and H. Kato, This Bulletin, **41**, 1031 (1968).

where $(rr|ss)$ and $(rr'|rr')$ are the two-center Coulomb and one-center exchange repulsion integrals respectively; where $\sum_{r'(\neq r)}^{\text{on A}}$ denotes the summation over all the valence AO's of the A atom except for the rth AO, and where the diagonal core integrals, H_{rr}, are given as follows:[1,5]

$$H_{rr} = U_{rr} + \sum_{B\neq A} (B|rr) \tag{2}$$

$$U_{rr} = -I_r - (N_r - 1)(rr|rr) - \sum_{r'(\neq r)}^{\text{on A}} N_{r'}\left[(rr|r'r') - \frac{1}{2}(rr'|rr')\right] \tag{3}$$

$$(B|rr) = -\sum_{s}^{\text{on B}} N_s(ss|rr) \tag{4}$$

where I_r is the valence state ionization potential of the rth AO and where N_r denotes the number of the valence electrons occupying the rth AO in the valence state. For the valence p AO, U_{rr} is taken as the average value fort he P_x, P_y, and P_z AO's on the same atom.

The off-diagonal elements of the Fock's operator are written in either of two ways, according to whether they are concerned with one-center or two-centers:

$$F_{rr'} = -\frac{1}{2}P_{rr'}\left[(rr|r'r') - 3(rr'|rr')\right]$$

($r\neq r'$, but both on the same atom) (5)

$$F_{rs} = H_{rs} - \frac{1}{2}P_{rs}(rr|ss)$$

($r\neq s$, on different atoms) (6)

where H_{rs} is the core resonance integral, which is given by the following two equations;

$$H_{rs} = -\frac{1}{2}KS_{rs}(I_r + I_s)$$

($r\neq s$, belonging to the adjacent atoms) (7)

$$H_{rs} = 0$$

(otherwise, but $r\neq s$)

where S_{rs} is the overlap integral between the rth and the sth AO's and where K is a constant taken to be 0.8 in the present calculation. This value will be discussed in the later part of this section. The overlap integrals are calculated with the Slater-type AO's, where the exponent values adopted are those obtained by Clementi and Raimondi[7] (shown in Table 1).

Table 1. Slater exponents (ζ_r) and valence state ionization potentials (I_r) of AO's and electron repulsion integrals

		ζ_r[a]	I_r,[b] eV	$(rr\|rr)$,[c] eV	$(rr'\|rr')$,[d] eV
H	1s	1.0000	13.60	12.85	
C	2s	1.6083	21.01	12.10	(2s2p|2s2p)=2.30
	2p	1.5679	11.27	10.93	(2p2p'|2p2p')=0.60
N	2s	1.9237	26.92	12.87	(2s2p|2s2p)=2.99
	2p	1.9170	14.42	11.88	(2p2p'|2p2p')=0.86
S	3s	2.1223	20.08	8.54	(3s3p|3s3p)=1.02
	3p	1.8273	13.32	9.82	(3p3p'|3p3p')=0.60

a) Ref. 7.
b) J. Hinze and H. H. Jaffé *J. Am. Chem. Soc.*, **84**, 540 (1962).
c) Evaluated from the values of I_r and E_r of Ref. b by Eq. (8).
d) Ref. 9.

The one-center Coulomb repulsion integrals are approximated as follows:

$$(rr|rr) = I_r - E_r \tag{8}$$

where E_r is the valence-state electron affinity of the rth AO. The one-center and two-center Coulomb repulsion integrals are calculated by the Ohno approximation:[8],*2

$$(rr|ss) = \frac{1}{2}(1/\sqrt{R_{rs}^2 + 1/(rr|rr)^2} + 1/\sqrt{R_{rs}^2 + 1/(ss|ss)^2}) \tag{9}$$

where R_{rs} is the distance between the atoms to which the two AO's blong.

The one-center exchange integrals are evaluated by the Slater-Condon parameters estimated by Hinze and Jaffé.[9] These values are listed in Table 1, together with the values of I_r and $(rr|rr)$.

For the geomtries of the treated molecules except for benzyne and hetarynes, the data compiled in Ref. 10 are used. An initial set of MO coefficients is obiained by putting F_{rr} as equal to $-I_r$ and by reducing F_{sr} to the H_{rs} term only. The iteration procedure is carried out until the variation in every MO energy remains within 0.001 eV.

Choice of Parameters. The value of K in Eq. (7), which is determined so that the lower calculated

Table 2. Calculated and the experimental π-π^* transition energies of benzene (eV)

State	Calcd	Obsd[a]
$^1B_{2u}$	5.00	4.89
$^1B_{1u}$	5.19	6.14
$^1E_{1u}$	7.36	6.76
$^3B_{2u}$	5.00	5.76
$^3B_{1u}$	4.04	3.66
$^3E_{1u}$	4.52	4.69

a) D. K. Kearns, *J. Chem. Phys.*, **36**, 1608 (1962).

7) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
8) K. Ohno, *Theroret. chim. Acta (Berl.)*, **2**, 219 (1964).
*2 When this approximation for the one-center integral (npnp–np'np') is adopted, the rotation invariance to local axes is not exactly preserved. The present results do not differ essentially from the improved results for benzene, pyridine, and benzyne. This improvement will be reported in the near future.
9) J. Hinze and H. H. Jaffé, *J. Chem. Phys.*, **38**, 1834 (1963).
10) "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. by L. E. Sutton, The Chem. Soc., London (1956 and 1965).

π–π^* transition energies of benzene fit the observed values, is 0.8. The π–π^* transition energies calculated with this value are cited in Table 2, together with the experimental values. This value is adopted throughout these calculations.

Results and Discussion

In this section, some calculated quantities of benzene, pyridine, pyrimidine, and thiophene, the parent molecules of the intermediates treated in this paper, will first be compared with those obtained by other methods of calculation and by other experiments. Second, an empirical relation between the calculated "bond energy" and the bond length will be presented in order to make it possible to estimate the unknown bond lengths of the intermediates. Finally, the electronic structures and configuration of benzyne and hetarynes will be discussed.

Benzene, Pyridine, Pyrimidine, and Thiophene. In Table 3, the occupied MO energies for benzene calculated by the present method are compared with the results of Schulman and Moskowitz[11] and with the experimental ionization potentials assigned by Lindholm and Jonsson.[12] In general, the values of the MO energies of the present calculations are lower than the others. However, the sequence of MO's obtained by our treatments is fairly consistent with the others.

Table 3. Occupied MO energies (eV) for benzene[a]

	Present calcd	Schulman and Moskowitz[b]	Obsd[c]
$e_{1g}(\pi)$	−11.28	−7.83	−9.3
e_{2g}	−13.04	−10.18	−11.4
$a_{2u}(\pi)$	−14.63	−12.30	−12.1
b_{2u}	−14.76	−12.20	−14.7
e_{1u}	−16.00	−12.87	−13.8
b_{1u}	−18.25	−15.31	−15.4
a_{1g}	−20.15	−15.53	−16.9
e_{2g}	−24.59	−19.43	−19.2
e_{1u}	−31.88	−24.42	—
a_{1g}	−36.30	−26.92	—

a) The notation (π) indicates a π molecular orbital.
b) Ref. 11.
c) Ref. 12.

For pyridine, our MO energies are in better agreement with those calculated by Clementi[13] and with the ionization potential measured by the photoionization experiment of Al-Joboury and Turner[14] than is the case with benzene, as is shown in Table 4. The highest occupied (HO) orbital is a nonbonding (n) one in our calculation; this is incompatible with the finding of Clementi[13] and the experimental assignment by Al-Joboury and Turner.[14,15]

Table 4. Occupied MO energies (eV) for pyridine[a]

	Present calcd	Clementi[b]	Obsd[c]
$a_1(n)$	−11.41	−12.66	−10.54
$a_2(\pi)$	−11.55	−12.17	−9.28
$b_1(\pi)$	−11.98	−12.47	−12.22
b_2	−13.49	−15.77	−13.43
$b_1(\pi)$	−15.13	−16.93	−14.44
a_1	−15.18	−17.40	−15.49
b_2	−15.44	−18.23	−16.94
b_2	−16.26	−19.75	−19.39
a_1	−18.09	−19.08	−20.14
a_1	−20.22	−21.20	
b_2	−24.79	−24.61	
a_1	−25.15	−25.08	
b_2	−32.02	−30.21	
a_1	−33.61	−35.50	
a_1	−38.12	−36.13	

a) (n) denotes a non-bonding (lone pair) orbital.
b) Ref. 13.
c) Ref. 14; The assignment of experimental values lower than −10.54 and −9.28 are not definite.

The occupied MO energies for pyridimidine

Table 5. Occupied MO energies (eV) for pyrimidine and thiophene

Pyrimidine		Thiophene	
$b_2(n)$	−11.34	$a_2(\pi)$	−11.00
$a_2(\pi)$	−12.12	$b_1(\pi)$	−11.44
$a_1(n)$	−12.35	$a_1(n)$	−12.78
$b_1(\pi)$	−12.48	a_1	−14.11
a_1	−15.34	b_2	−14.13
b_2	−15.46	$b_1(\pi)$	−14.91
$b_1(\pi)$	−15.58	b_2	−15.43
b_2	−16.18	a_1	−17.47
a_1	−17.66	a_1	−20.75
a_1	−20.43	b_2	−22.34
a_1	−25.14	a_1	−27.37
b_2	−25.56	b_2	−30.37
a_1	−32.94	a_1	−35.35
b_2	−35.22		
a_1	−39.17		

11) J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **43**, 3287 (1965).
12) E. Lindholm and B.-Ö. Jonsson, *Chem. Phys. Letters*, **1**, 501 (1967).
13) E. Clementi, *J. Chem. Phys.*, **46**, 4731 (1967).
14) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.
15) By a slight modification of the parametrization, the highest occupied orbital becomes a π MO. This improvement will be described in the near future.

and thiophene, are presented in Table 5. The n orbital of thiophene, localizing mainly on the sulfur atom, is more stable than the higher π orbitals.

The transition energies were calculated for various types of excitations. The calculated values of the π–π^* and n–π^* types for pyridine, pyrimidine, and thiophene are given in Table 6, together with the experimental values. The configuration interactions, including all the π–π^* and n–π^* singly-excited states, are, further, taken into account. When the configuration interactions are considered, a fair agreement between the calculated and observed transition energies and oscillator strengths is observed. The energies of the first π–π^* transitions,

TABLE 6. CALCULATED TRANSITION ENERGIES (eV) OF PYRIDINE, PYRIMIDINE AND THIOPHENE

(a) Pyridine

Transition	State	Calcd (f)	Calcd +SECI (f)	Obsd[a] (f)
n–π^*	$^1B_1$	4.20(0.0002)	3.97(0.0007)	4.31(0.003)
n–π^*	$^1A_2$	4.74(0)	—	—
π–π^*	$^1B_2$	5.83(0.53)	4.95(0.02)	4.75(0.04)
π–π^*	$^1A_1$	6.30(0.57)	4.99(0.0001)	6.17(0.10)
π–π^*	$^1B_2$	6.45(0.50)	7.32(1.19)	6.82(1.3)
π–π^*	$^1A_1$	6.37(0.58)	7.45(1.35)	
n–π^*	$^3B_1$	3.82(0)	3.50(0)	—
n–π^*	$^3A_2$	4.66(0)	—	—
π–π^*	$^3A_1$	4.28(0)	3.58(0)	3.68
π–π^*	$^3B_2$	4.35(0)	4.29(0)	—

(b) Pyrimidine

Transition	State	Calcd (f)	Calcd +SECI (f)	Obsd[a] (f)
n–π^*	$^1B_1$	3.66(0.0009)	3.52(0.002)	3.85(0.007)
n–π^*	$^1A_2$	4.15(0)	4.06(0)	—
n–π^*	$^1B_1$	5.16(0.0005)	5.08(0.001)	6.34(0.005)?
π–π^*	$^1B_2$	5.90(0.56)	4.94(0.02)	5.00(0.05)
π–π^*	$^1A_1$	6.20(0.49)	5.04(0.04)	6.49(0.16)?
π–π^*	$^1A_1$	6.31(0.48)	7.23(1.12)	7.25(1.0)
π–π^*	$^1B_2$	6.52(0.52)	7.45(1.24)	
n–π^*	$^3B_1$	3.39(0)	3.15(0)	3.63 —
n–π^*	$^3A_2$	4.00(0)	3.72(0)	—
π–π^*	$^3A_1$	4.25(0)	3.57(0)	—
π–π^*	$^3B_2$	4.30(0)	4.23(0)	—

(c) Thiophene

Transition	State	Calcd (f)	Calcd +SECI (f)	Obsd (f)
π–π^*	$^1B_2$	5.81(0.41)	5.50(0.23)	5.16—5.90[b] (0.1)[c]
π–π^*	$^1A_1$	6.39(0.62)	6.04(0.16)	6.59—7.25[b] —
π–π^*	$^1A_1$	7.39(0.47)	7.71(1.05)	—
π–π^*	$^1B_2$	7.69(0.17)	7.87(0.41)	—
n–π^*	$^1B_1$	6.37(0.008)	—	—
n–π^*	$^1A_2$	8.58(0)	—	—
π–π^*	$^3B_2$	3.81(0)	3.37(0)	3.89—3.96[d]
π–π^*	$^3A_1$	4.84(0)	4.32(0)	—
n–π^*	$^3B_1$	6.18(0)	—	—
n–π^*	$^3A_2$	8.45(0)	—	—

a) K. K. Innes, J. P. Byrne and I. G. Ross, *J. Mol. Spectroscopy*, **22**, 125 (1967).
b) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.*, **A179**, 201 (1941).
c) J. Sicé *J. Phys. Chem.* **64**, 1572 (1960).
d) M. R. Padbye and S. R. Desai, *Proc. Phys. Soc.*, **A65**, 298 (1952).

$^1A_1 \rightarrow {}^1A_1$, in pyridine and pyrimidine do not agree with the experimental results. These transitions in pyridine and pyrimidine can be correlated with the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition in benzene, the transition energy of which is also in poor agreement with the experimental results, as may be seen in Table 2.

Table 7. AO Charge density for pyridine[a)]

		Present calcd	Clementi[b)]
N	2s	1.561	1.5090
	$2p_x$	0.981	1.0486
	$2p_y$	1.702	1.6608
	$2p_z$	1.183	1.0102
C_2	2s	1.221	1.0472
	$2p_x$	0.793	1.0436
	$2p_y$	0.839	1.0149
	$2p_z$	0.898	1.0048
C_3	2s	1.247	1.0657
	$2p_x$	0.890	1.1138
	$2p_y$	0.911	1.0441
	$2p_z$	1.046	1.0024
C_4	2s	1.245	1.0722
	$2p_x$	0.889	1.0110
	$2p_y$	0.888	1.1444
	$2p_z$	0.931	0.9755
H_2	1s	1.006	0.7783
H_3	1s	0.968	0.7829
H_4	1s	0.986	0.7797

a) y axis is taken as C_2 rotation axis; z axis is taken perpendicular to plane of a molecule.
b) Ref. 13.

Table 8. AO Charge density for pyrimidine and thiophene

Pyrimidine[a)]			Thiophene[a)]		
N	2s	1.578	S	3s	1.702
	$2p_x$	1.489		$3p_x$	1.123
	$2p_y$	1.197		$3p_y$	1.553
	$2p_z$	1.230		$3p_z$	1.755
C_2	2s	1.185	C_2	2s	1.248
	$2p_x$	0.686		$2p_x$	0.835
	$2p_y$	0.823		$2p_y$	0.788
	$2p_z$	0.791		$2p_z$	1.045
C_4	2s	1.225	C_3	2s	1.246
	$2p_x$	0.883		$2p_x$	0.883
	$2p_y$	0.756		$2p_y$	0.876
	$2p_z$	0.828		$2p_z$	1.078
C_5	2s	1.248	H_2	1s	0.974
	$2p_x$	0.923	H_3	1s	0.961
	$2p_y$	0.902			
	$2p_z$	1.093			
H_2	1s	1.021			
H_4	1s	1.002			
H_5	1s	0.950			

a) y is taken as C_2 rotation axis; z is taken perpendicular to plane of a molecule.

These discrepancies may partly be attributed to the evaluation of the two-center Coulomb repulsion by Ohno approximation.[8)] The lowest n–π^* transition energy in thiophene is calculated to be larger than those in pyridine and pyrimidine, and it is also larger than some π–π^* transition energies in thiophene. The fact that the n–π^* transition in thiophene has never been observed may be evidence supporting the present results.

The AO-charge densities for pyridine calculated by the present method are compared with those obtained by Clementi[13)] in Table 7. The formal charge on the nitrogen atom becomes -0.426 in the present calculation, while it was obtained as -0.229 by Clementi.[13)] It may be noted that the large negative charge on the nitrogen atom in the present results is supplies mainly by the σ electrons rather than by the π electrons (the $2p_z$ orbitals in Table 7). The AO-charge densities for pyrimidine and thiophene are also given in Table 8. The $2p_\pi$ AO-charge and atomic charges of the nitrogen atom in pyrimidine are both larger than those in pyridine. This trend for the π charges in two compounds coincides with the finding of McWeeny and Peacock.[16)] The formal charge of the sulfur atom in thiophen, in spite of a considerably large positive value of the $3p_\pi$ net charge, is negative as a result of the back-donation of the σ electrons.

The molecular dipole moments are given approximately by the vector sum of the moment, μ_Q, derived from the net atomic charge and by the atomic dipole moment, μ_{atom}.[17)] The z components in the appropriate Cartesian coordinate are given in Debye units by using Slater-type AO's:

$$\mu_Q(z) = 4.8030 \sum_{A}^{atoms} Q_A z_A$$

$$\mu_{atom(z)} = -\sum_{A}^{atoms} D_n(A) \cdot P_{ns(A)np_z(A)} \times [\zeta_s(A) \cdot \zeta_p(A)]^{n+1/2} \Big/ \left[\frac{\zeta_s(A)+\zeta_p(A)}{2}\right]^{2n+2}$$

where z_A is the z coordinate of the A atom given in units of Å, where $P_{ns(A)np_z(A)}$ is the bond order between the ns and np_z AO's of the A atom, where ζ_s and ζ_p are the orbital exponents for the s and p atomic orbital functions, and where $D_n(A)$ is the constant which is common to the nth row elements, *i. e.*, for $n=2$ and $n=3$, $D_2=7.3370$ Debye and $D_3=10.2718$ Debye. The calculated dipole moments for pyridine and pyridimidine are in fair agreement with the experimental values shown in Table 9. The large calculated dipole moment for thiophene shows that there is still some room for improvement.

16) R. McWeeny and T. E. Peacock, *Proc. Phys. Soc.*, **A70**, 41 (1957).
17) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, s136 (1965).

TABLE 9. CALCULATED AND OBSERVED DIPOLE MOMENTS (Debye)

	Calcd			Obsd
	μ_Q	μ_{atom}	μ_{total}	μ
Pyridine	1.50	0.78	2.28	2.20[a]
Pyrimidine	1.78	0.91	2.69	2.42[a]
Thiophene	0.49	1.41	1.90	0.55[b]

a) Y. Morino, "Constants of Organic Compounds," Asakura Pub., Tokyo (1963), p. 500.
b) B. Harris, R. J. Le Févre and E. P. A. Sullivan, *J. Chem. Soc.*, **1953**, 1622.

Relation Between Bond Length and E_{AB}. A bond length-bond order relation is usually used to estimate the unknown bond lengths in a π electron approximation.[18] The σ electron contribution is considered to be a constant for every bond in these treatments. In the present paper, a graphical procedure to estimate the bond length of a bond by considering all the valence electrons explicitly is proposed. For this purpose, we utilize the total electronic energy, E_{AB}, of the AB bond as given in Eq. (10) instead of the bond order:

$$E_{AB} = \sum_{r}^{\text{on A}} \sum_{s}^{\text{on B}} P_{rs}(H_{rs}+F_{rs}) \tag{10}$$

Here $\sum_{r}^{\text{on A}}$ denotes the summation over all the valence AO's belonging to the A atom. We first plot the E_{AB} values *vs.* the observed carbon-carbon bond lengths, R_{AB}, for some typical molecules (for example, C_2H_6, C_2H_4, C_6H_6, and C_2H_2) and also for pyridine, pyrimidine, and thiophene. As may be seen in Fig. 1, a fairly smooth curve can be drawn, and this curve may then be used to predict the lengths of a bond as a semi-empirical relation according to π electron theory. The curves for carbon-nitrogen and carbon-sulfur bonds are obtained similarly (Figs. 2 and 3). These semi-empirical curves will be employed to estimate the bond lengths of benzyne and hetarynes in the next section.

Benzyne and Hetarynes. Benzyne is also called dehydrobenzene and is known to be a typical unstable intermediate on the basis of many experimental results.[19] The electronic structure of benzyne has been discussed from several points of

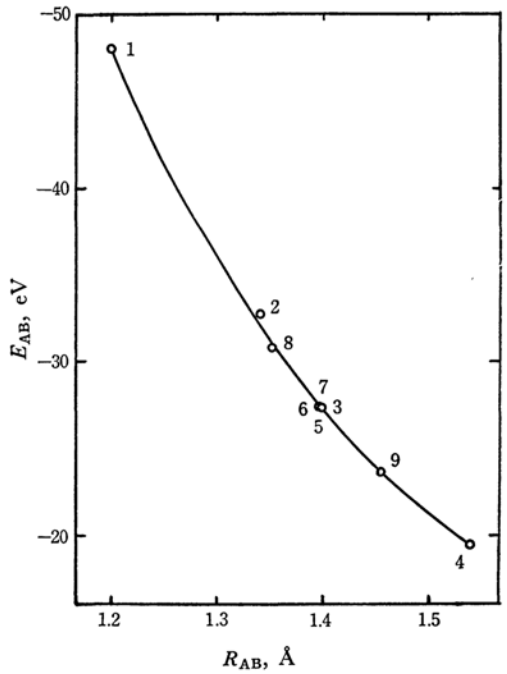

Fig. 1. Values of E_{AB} *vs.* R_{AB} for the carbon-carbon bonds.
1: acetylene 2: ethylene 3: benzene
4: ethane 5: pyridine (2-3)
6: pyridine (3-4) 7: pyrimidine
8: thiophene (2-3) 9: thiophene (3-4)

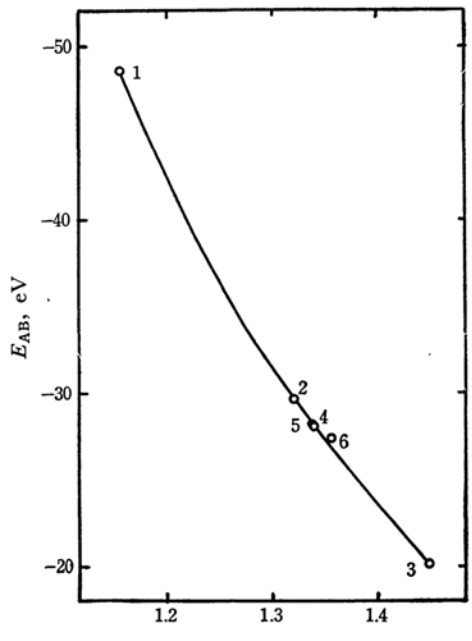

Fig. 2. Values of E_{AB} *vs.* R_{AB} for the carbon-nitrogen bonds.
1: hydrogen cyanide 2: diazomethane
3: methylamine 4: pyridine
5: pyrimidine (1-2) 6: pyrimidine (3-4)

18) C. A. Coulson, *Proc. Roy. Soc.*, **A169**, 413 (1939); for a recent example, *cf.* M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44**, 759 (1966).

19) H. Heaney, *Chem. Revs.*, **62**, 81 (1962).

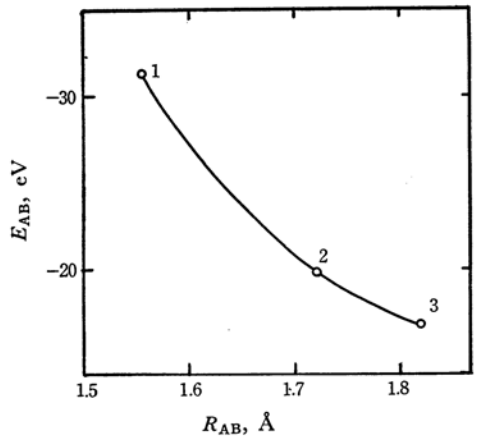

Fig. 3. Values of E_{AB} *vs.* R_{AB} for the carbon-sulfur bonds.
1: carbon disulfide 2: thiophene 3: methyl mercaptan

view by several authors,[20-24] but the electron interation has never explicitly been taken into account in these treatments. Hetarynes and benzyne analogues derives from heteroaromatic compounds, such as 3,4-pyridyne,[25,26] 4,5-pyrimidyne,[25,27] and 2,3-thiophyne,[28] may also be supposed to be unstable intermediates. Calculations on these intermediates and their isomers are performed using the semi-empirical SCF MO method presented in this paper.

Benzyne and hetarynes are so unstable that no information on their geometrical structures has ever been obtained by any experiments. An attempt to estimate the bond lengths of benzyne was made by Coulson by means of a π electron calculation of the Hückel type.[20] He used a semi-empirical bond length-bond order relation. In the present paper, we will use other semiempirical curves relating the bond lengths to the E_{AB}[6]

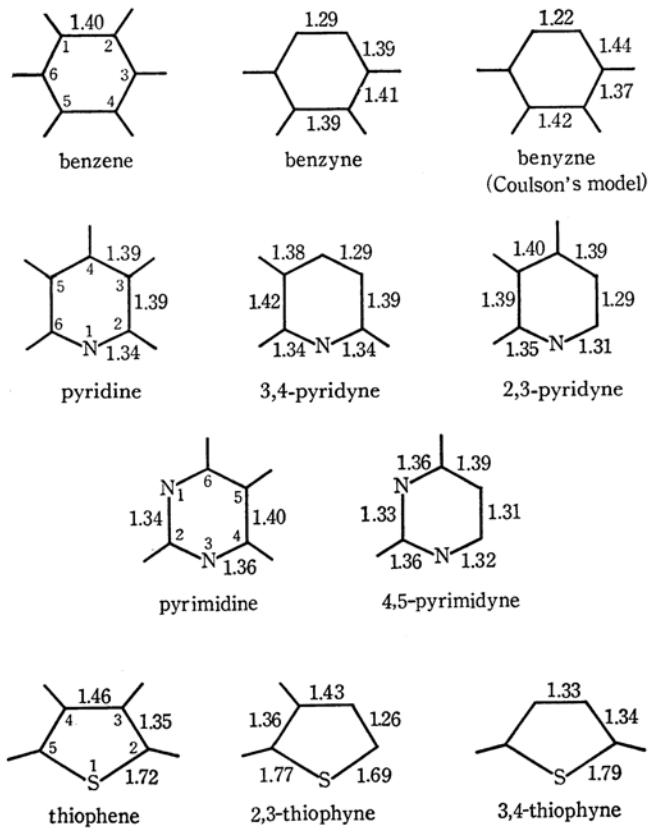

Fig. 4. SCF bond lengths of benzyne and hetarynes.

20) C. A. Coulson, *Chem. Soc. Special Publ. (London)*, **12**, 100 (1958).
21) H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).
22) R. Huisgen, "Organometallic Chemistry," ed. by H. Zeiss, Reinhold, N. Y. (1960), p. 36.
23) T. Yonezawa, H. Konishi, H. Kato, K. Morokuma and K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 869 (1966).
24) R. Hoffmann, A. Imamura and W. J. Hehre, *J. Am. Chem. Soc.*, **90**, 1499 (1968).
25) Th. Kauffmann, *Angew. Chem.*, **77**, 557 (1965).
26) Th. Kauffmann and F.-P. Boettcher, *Chem. Ber.*, **95**, 1528 (1962).
27) H. C. van der Plas, *Tetrahedron Letters*, **1965**, 555.
28) G. Wittig, *Angew. Chem.*, **74**, 479 (1962).

(Figs. 1—3).

First, the geometry of the parent molecule with two hydrogen atoms eliminated is adopted for that of an intermediate, and calculation is carried out; secondly, all the bond lengths except for the carbon-hydrogen bonds are estimated at each iteration by using the relation shown in Figs. 1—3. In the course of these iterations, the planarity of a molecule and minimum changes in the bond angles were assumed. The iteration is repeated until a self-consistency within 0.01 Å between the input and the output bond lengths is established.

The SCF bond lengths of the carbon-carbon, the carbon-nitrogen, and the carbon-sulfur bonds in benzyne and hetaynes are shown, together with those of their parent molecules for the sake of comparison, in Fig. 4. The bonds from which the two hydrogen atoms are removed become shorter by about 0.1 Å than parent molecules and take values intermediate between those of the double and triple bonds. For benzyne, the bond lengths estimated by Coulson[20] are also presented in Fig. 4. The present results differ from those of Coulson to some extent. The value of the shortest bond by Coulson is very close to that of the triple bond in acetylene, while our shortest bond is not so short.

The π charge densities for benzyne and hetarynes are presented in Table 10. The variations in the π-charge densities from their parent molecules are not very large except for the C_5 position in 4,5-pyrimidyne.

The values of the π and π' bond orders for benzyne, hetarynes, and their parent molecules in Table 11 show that the shortest bonds of benzyne and hetarnes have quite large $P_{\pi'\pi'}$ values, values which are rather larger than the $P_{\pi\pi}$ values. The total π bond order, the sums of $P_{\pi\pi}$ and $P_{\pi'\pi'}$ for these bonds range from 1.3 to 1.7. From the findings on the bond lengths and the total π bond orders for the shortest carbon-carbon bonds of benzyne and hetarynes, these bonds seem to be normal triple bonds, which may have slightly different bond characters.

It may be noted that all the HO orbitals of

Table 10. π Charge densities for benzyne and hetarynes

a) Benzyne

C_1	C_3	C_4
0.959	1.025	1.016

b) 3,4-Pyridyne

N_1	C_2	C_3	C_4	C_5	C_6
1.217	0.898	0.965	0.913	1.076	0.930

c) 2,3-Pyridyne

N_1	C_2	C_3	C_4	C_5	C_6
1.218	0.931	0.932	0.953	1.038	0.928

d) 4,5-Pyrimidyne

N_1	C_2	N_3	C_4	C_5	C_6
1.191	0.833	1.219	0.760	1.285	0.731

e) 2,3-Thiophyne

S_1	C_2	C_3	C_4	C_5
1.788	0.954	1.104	1.059	1.095

f) 3,4-Thiophyne

S_1	C_2	C_3
1.803	1.089	1.010

Table 11. Values of π and π' bond orders for benzyne, hetarynes and their parent molecules

Bond		$P_{\pi\pi}$	$P_{\pi'\pi'}$*
Benzene	1-2	0.667	—
Benzyne	1-2	0.700	0.819
Pyridine	3-4	0.665	—
Pyridine	2-3	0.667	—
3,4-Pyridyne	3-4	0.700	0.803
2,3-Pyridyne	2-3	0.694	0.770
Pyrimidine	4-5	0.667	—
4,5-Pyrimidyne	4-5	0.690	0.715
Thiophene	2-3	0.853	—
Thiophene	3-4	0.451	—
2,3-Thiophyne	2-3	0.865	0.815
3,4-Thiophyne	3-4	0.483	0.793

* The notation π' represents the component of p orbital which lies in the molecular plane and is perpendicular to the bond axis.

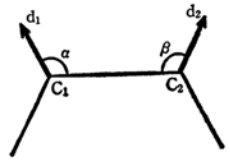

Fig. 5. Directions of the partial atomic dipoles of the carbon atoms in the molecular plane. C_2 is near to a heteroatom in hetaryne.

Table 12. Moments of the partial atomic dipoles of the carbon atoms in the HO and LV orbitals and the angles α and β[a]

		$\lvert d_1\rvert$	$\lvert d_2\rvert$	α(°)	β(°)
Benzyne	HO	0.74	0.74	133	133
	LV	1.31	1.31	123	123
3,4-Pyridyne	HO	0.28	1.38	136	140
	LV	1.34	1.10	122	123
2,3-Pyridyne	HO	1.14	0.01	135	133
	LV	1.19	1.60	121	118
4,5-Pyrimidyne	HO	1.43	0.00	138	141
	LV	0.40	1.90	109	124
2,3-Thiophyne	HO	0.56	0.87	133	134
	LV	1.52	1.73	119	142
3,4-Thiophyne	NHO*	0.76	0.76	128	128
	LV	1.14	1.14	127	127

a) The definition of d_1, d_2, α and β are illustrated in Fig. 5.

* NHO: the next highest orbital.

benzyne and hetarynes except for 3,4-thiophyne and the lowest vacant (LV) orbitals of all the intermediates are highly localized on the carbon atoms from which the two hydrogen atoms are removed. We calculated the partial atomic dipole, d_i, of the ith carbon atom of the triple bond in these MO's. The absolute values of the d_1 and d_2 vectors the α and β angles of the orientation of the partial atomic moment from the C_1–C_2 axis (in Fig. 5) are given in Table 12. The large absolute values of d_1 and d_2 show that the electrons of these MO's are considerably localized at these carbon atoms and that the centers of the negative charge are far from the atom. The values of α and β, which are about 120°, indicate that the HO and LV MO's of benzyne and hetarynes may be described approximately as a linear combination of non-bonding sp^2-type hybrids of the carbon atoms, as has been pointed out by Ingold and King[29] for the excited bent acetylene.

It is well known that benzyne and hetarynes react as intermediates with nucleophilic reagents in the elmination-addition reaction of some substituted benzene and heterocyclic compounds.[19,25] The reactions of hetarynes with nucleophilic reagents generally afford two kinds of isomeric products. The main product of isomers may be predicted from the charge distributions in the LV orbitals of hetarynes. The absolute values of the partial atomic dipole moments in Table 12, which represent the relative strengths of the σ electron-donating power of each carbon atom of the triple bond, can be employed in the present case. From

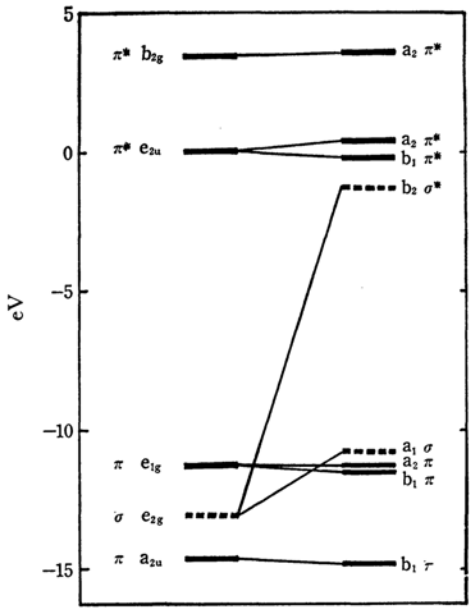

Fig. 6. Relation between the MO levels of benzene and benzynes. The full lines indicate the π MO levels and the dotted line are σ MO levels.

29) C. K. Ingold and G. W. King, *J. Chem. Soc.*, **1953**, 2702.

Table 13. Calculated transition energies (eV) of benzyne and hetarynes

Transition	state	(f)	+SECI(f)
Benzyne			
σ–σ^*	$^1B_2$	3.73(0.28)	3.01(0.05)
π–σ^*	$^1A_2$	3.63(0)	3.33(0)
π–σ^*	$^1B_1$	3.57(0.0003)	3.54(0.0003)
π–π^*	$^1B_2$	6.13(0.57)	4.87(0.03)
π–π^*	$^1A_1$	6.13(0.51)	5.12(0.005)
σ–σ^*	$^3B_2$	1.65(0)	1.24(0)
π–π^*	$^3B_2$	4.01(0)	3.56(0)
π–π^*	$^3A_1$	4.70(0)	4.59(0)
3,4-Pyridyne			
σ–σ^*	$^1A'$	3.44(0.20)	2.96(0.05)
n–π^*	$^1A''$	5.02(0.0001)	4.66(0.001)
π–π^*	$^1A'$	5.91(0.53)	5.04(0.03)
π–π^*	$^1A'$	6.17(0.49)	6.06(0.31)
σ–σ^*	$^3A'$	1.82(0)	1.67(0)
π–π^*	$^3A'$	4.13(0)	3.59(0)
n–π^*	$^3A''$	4.68(0)	4.14(0)
2,3-Pyridyne			
σ–σ^*	$^1A'$	3.13(0.21)	2.68(0.05)
π–π^*	$^1A'$	5.76(0.48)	4.93(0.03)
π–π^*	$^1A'$	6.27(0.57)	5.07(0.03)
n–π^*	$^1A''$	5.95(10^{-9})	5.57(0.0001)
σ–σ^*	$^3A'$	1.60(0)	1.42(0)
π–π^*	$^3A'$	4.10(0)	3.57(0)
n–π^*	$^3A''$	5.64(0)	5.13(0)
4,5-Pyrimidyne			
σ–σ^*	$^1A'$	2.56(0.11)	2.25(0.02)
n–π^*	$^1A''$	4.78(10^{-5})	4.61(0.002)
π–π^*	$^1A'$	5.72(0.53)	4.99(0.04)
π–π^*	$^1A'$	6.21(0.43)	5.34(0.01)
σ–σ^*	$^3A'$	1.46(0)	1.33(0)
π–π^*	$^3A'$	3.87(0)	3.53(0)
n–π^*	$^3A''$	4.54(0)	3.95(0)
2,3-Thiophyne			
σ–σ^*	$^1A'$	2.80(0.11)	2.34(0.03)
π–π^*	$^1A'$	5.87(0.38)	5.85(0.28)
π–π^*	$^1A'$	6.57(0.55)	6.33(0.16)
n–π^*	$^1A''$	6.75(0.003)	6.48(0.002)
σ–σ^*	$^3A'$	0.85(0)	0.76(0)
π–π^*	$^3A'$	3.99(0)	3.49(0)
n–π^*	$^3A''$	6.57(0)	6.68(0)
3,4-Thiophyne			
σ–σ^*	$^1B_2$	2.91(0.18)	2.65(0.09)
π–π^*	$^1B_2$	5.54(0.49)	5.34(0.47)
π–π^*	$^1A_1$	6.30(0.51)	6.06(0.21)
n–π^*	$^1B_1$	6.19(0.005)	6.20(0.005)
σ–σ^*	$^3B_2$	0.86(0)	0.84(0)
π–π^*	$^3B_2$	3.28(0)	2.98(0)
n–π^*	$^3B_1$	6.01(0)	6.02(0)

the present calculation, the more reactive sites may be predicted to be as follows: the 4 site for 3,4-pyridyne; the 2 site for 2,3-pyridyne; the 4 site for 4,5-pyrimidyne and the 2 site for 2,3-thiophyne. The only experimental results available for comparison are for 3,4-pyridyne[26] and 4,5pyrimidyne.[25] The reactions of 3-chloro and 3-bromopyridine with lithium piperidide and piperidine give 3- and 4-piperidinopyridine in the 48 : 52 ratio.[25] For the case of 4,5-pyrimidyne, only 4-piperidinopyrimidine was obtained under the same conditions.[25] These experimental results support the predictions based on the present calculations.

Some molecular orbital energy levels of benzyne are illustrated in Fig. 6, combined with those of benzene. The HO and LV orbitals of benzyne are σ-type orbitals (mentioned above), which become unstable because they lack the two hydrogen atoms. The energy changes of the π orbitals are small. The occupied π orbitals of benzene become slightly stable, and also the degeneracy is removed. The other occupied σ-type orbitals of benzyne are more unstable than the corresponding σ orbitals of benzene. Analogous situations also occur in the case of each hetaryne.

The transition energies of benzyne and hetarynes have been calculated, and the configuration interactions further considered among a limited number of singly-excited configurations.[30] The calculated lowest singlet transitions in benzyne and hetarynes, shown in Table 13, are all σ–σ^* type transitions, from the HO to the LV levels. As the experimental value for benzyne, the value of 4.9 eV assigned to the π–π^* transition with the oscillator strength of magnitude of 0.1—0.2[31] has been reported. This energy of the transition is near the value of the lowest singlet π–π^* transition for benzene; this is also shown by the present calculations. The calculated lowest transition energies of the n–π^* type for hetarynes indicate the blue shifts referred to the corresponding ones of their parent molecules (*cf.* Table 6). In addition, the larger shift in 2,3-pyridyne than in 3,4-pyridyne can be recognized. This result may be due to the stronger interaction between the lone pair on the heteroatom and the non-bonding sp^2-type hybrids on the carbon atoms, which are situated nearer each other in the case of 2,3-piridyne than in that of 3,4-pyridyne. A similar tendency is found in the cases of 2,3-thiophyne and 3,4-thiophyne.[32]

A benzyne structure with a triplet state in its ground state was long ago discussed by Müller and Röscheisen,[33] but it was pointed out to be unlikely by Huisgen.[22] In the present calculations, the lowest triplet transitions for benzyne and hetarynes are π–π^*-type transitions. The calculated values for these transitions in Table 13 are extraordinarily small, but they are not negative; therefore, the lowest triplet states of benzyne and hetarynes may lie very close to the ground states, which should be the singlet state.[34]

We are grateful to Professor I. Tabushi for his kind discussion and also to the computation centers of both Tokyo University and Kyoto University, where the present calculations were carried out.

30) The following numbers of configurations, which consist of two groups of AO's (n, π and HO; LV and π^*), are considered: 16 for benzyne; 20 for pyridynes; 24 for pyrimidyne; 15 for thiophynes.

31) R. S. Berry, G. N. Spokes and R. M. Stiles, *J. Chem. Soc.*, **82**, 5240 (1960); **84**, 3570 (1962).

32) In the present calculations, 3,4-pyridyne and 3,4-thiophyne become more stable than 2,3-pyridyne and 2,3-thiophyne respectively, while 2,3-thiophyne has been pointed out by Wittig to be more stable than 3,4-thiophyne (Ref. 28). This disagreement may be attributed to the total energy of the isomers of pyridynes and thiophynes obtained by the point-charge approximation for the core-core repulsion energy.

33) E. Müller and G. Röscheisen, *Chem. Ztg.*, **80**, 101 (1956).

34) Recently, benzyne in the triplet state has been found to make an appreciable contribution in a reaction of benzyne with substituted ethylenes: I. Tabushi, R. Oda and K. Okazaki, *Tetrahedron Letters*, **1968**, 3743.