May, 1973] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1301—1305 (1973) 1301

The SCF Screened Potential in π-Electron Systems

Toshitaka Terasaka, Taizo Iijima,* Yuichi Fujimura, and Takeshi Nakajima
Department of Chemistry, Faculty of Science, Tohoku University, Sendai

(Received May 24, 1972)

The screened potentials in π-electron systems have been calculated using the SCF orbitals and energies, and compared with Little's screened potentials calculated using the Hückel orbitals and energies. The characteristics of the screened potentials in benzenoid and nonbenzenoid aromatic hydrocarbons and in linear polyenes have been studied. It has been found that the use of the screened potential brings about considerable improvements in the triplet excitation energies in particular.

Recently, Gutfreund and Little[1,2] calculated the screened potential in the π-electron system of large conjugated molecules by means of the Random-Phase-Approximation (RPA) method,[3] which is familiar in the field of many-body physics. They have shown that, in the case of a π-electron system, the integral equation for the screened potential becomes a set of linear algebraic equations within the framework of the LCAO approximation. The results of a Hückel calculation are used in the algebraic equations to generate the screened potential, and with this potential an SCF calculation is performed. The excitation energies are calculated using the modified configuration-interaction (CI) method, in which a screened potential different from that used in the ground-state calculation is employed. The main results that they obtained are as follows: First, the qualitative behavior of the screened potential in the π-electron system is notably different from that in a metal or in an electron gas. In the metal and electron gas, the Coulomb potential of a test charge is effectively screened and behaves like $e^{-\lambda r}e^2/r$, where λ is of the order of several angstroms. On the other hand, in the π-electron system, the screened potential at sufficiently large distances exceeds the bare potential (that is, an antiscreening effect). Second, the screened potential shows a position dependence, although the bare potential does not. As a result, the Coulson-Rushbrooke theorem, which states that, in alternant hydrocarbons, the π-electron densities for all the carbon atoms are unity, does not generally hold for the SCF states calculated using the screened potential. Third, both singlet and triplet excitation energies calculated using the modified CI method assuming the screened potential agree more significantly well with the experimental values than do those calculated assuming the bare potential.

In the usual Pariser-Parr-Pople-type SCF calculation, the wavefunctions are determined by the Hartree-Fock potential, and *vice versa*, but the bare potential (consisting of one- and two-center repulsion integrals) is fixed through the SCF process. We wish to propose the following procedure for calculating the screened potential in π-electron systems using the SCF molecular-orbital wavefunctions and energies (this is the main purpose of this paper): at each step of an SCF calculation, let the screened potential be evaluated by the use of the wavefunctions and orbital energies obtained in that step, and then let us proceed to the next step using this screened potential. We call such a screened potential "the SCF screened potential", and the screened potential evaluated using the results of a Hückel calculation, "the Hückel screened potential".

We apply the above procedure to the SCF screened potential in combination with the variable bond-length SCF method,[4] which is known to reproduce well the equilibrium configurations of π-electron systems, to benzenoid and nonbenzenoid aromatic hydrocarbons, and to linear polyenes. We are concerned mainly with the following points: (1) the difference between the Hückel and SCF screened potentials; (2) the variation in the screened potential with respect to the sizes and forms of molecules, and (3) the position-dependence of the screened potential in the above molecules.

Theory

In the RPA method, the integral equation for the screened potential, V, has the following form:[1]

$$V(r_1, r_2, \omega) = V_0(|r_1-r_2|) + \iint \mathrm{d}r\mathrm{d}r' V_0(|r_1-r|)\pi_0(r, r', \omega)V(r', r_2, \omega), \quad (1)$$

where r_1, r_2, r, and r' are the coordinates of carbon atoms, where V_0 is the bare potential, where ω has the dimension of energy, and where the RPA polarization part, π_0, is given in terms of the single Green function, G_0, as:

$$\pi_0(r, r', \omega) = 2i\int\frac{d\omega'}{2\pi}G_0(r, r', \omega')G_0(r', r, \omega'-\omega). \quad (2)$$

In π-electron systems, the integral Eq. (1) becomes the following set of linear algebraic equations within the framework of the LCAO approximation:

$$V(r_1, r_2, \omega) = V_0(|r_1-r_2|) + \sum_m K(r_1, r_m, \omega)V(r_m, r_2, \omega), \quad (3)$$

where:

$$\begin{aligned} K(r_1, r_m, \omega) &= \sum_n V_0(|r_1-r_n|)\pi_0(r_n, r_m, \omega) \\ &= \sum_n V_0(|r_1-r_n|)\sum_{ia} 4\varepsilon_{ia}u_{ia}(r_n)u_{ia}(r_m)/(\omega^2-\varepsilon_{ia})^2, \\ \varepsilon_{ia} &= \varepsilon_i - \varepsilon_a, \qquad u_{ia}(r_n) = C_{in}C_{an}, \end{aligned} \quad (4)$$

---

* Present address: Chisso Co., Ltd., Goi, Chiba.

[1] H. Gutfreund and W. A. Little, *Phys. Rev.*, **183**, 68 (1969).

[2] H. Gutfreund and W. A. Little, *J. Chem. Phys.*, **50**, 4468 (1969).

[3] Leo P. Kadanoff and Gordon Baym, "Quantum Statistical Mechanics," W. A. Benjamin, Inc., New York, (1962).

[4] H. Yamaguchi, T. Nakajima, and T. Kunii, *Theoret. Chim. Acta* (Berl.), **12**, 349 (1968).

where ε_i denotes the orbital energy, C_{in}, the atomic-orbital coefficient in a molecular orbital, and the Latin and Greek indices, the unoccupied and occupied orbitals respectively. The screened potential is given in the matrix notation:

$$V(\omega) = [I-K(\omega)]^{-1}V_0, \tag{5}$$

where I is the unit matrix.

The screened potential in the ground state is calculated using Eq. (5), with $\omega=0$.

Method of Calculation

In this section, we shall briefly outline the following four procedures for use in calculating the screened potentials in the ground states of π-electron systems.

(1) Little's procedure¹⁾ (the Hückel screened potential): The Hückel molecular-orbital wavefunctions and energies are used to evaluate the screened potential, and an SCF calculation is then carried out using this screened potential.

(2) A procedure that combines Procedure (1) with the variable bond-length SCF method:⁴⁾ at each step of an SCF calculation, the C–C bond lengths (r) are evaluated from the corresponding bond orders (p) by the use of the relation between r and p, r (Å)$=1.520-0.186p$. Next, the Hückel-type calculation is performed using the core resonance integral which is given by $\beta(r)=(1.397/r)^4\beta(1.397)$.⁵⁾ The screened potential is evaluated using the results of the Hückel-type calculation. Using this screened potential, we carry out the next step of the SCF calculation. The process is repeated until self-consistency with respect to the total energy of the ground state is reached.

(3) The screened potential is evaluated at each step of the SCF calculation (the SCF screened potential). Using the molecular orbitals and orbital energies obtained after an iteration of the SCF calculation, we evaluate the screened potential. This screened potential is taken as the potential for the next iterative SCF calculation. The iteration is continued until self-consistency is reached. Notice that, in Procedure (1), the SCF calculation is carried out using a constant Hückel screened potential, while, on the other hand, in Procedure (3), the SCF calculation is carried out using a variable SCF screened potential.

(4) A procedure that combines Procedure (3) with the variable bond-length method. As in the second procedure, at each step of the SCF calculation, the new bond lengths are obtained from the corresponding bond orders. The screened potential is evaluated by means of the bare potential obtained from the new bond lenghts. This screened potential is used in the calculation of the next step. The calculation is repeated until self-consistency is reached.

Results and Discussion

First, let us compare the two kinds of Hückel screened potentials obtained using two different types of bare potentials, the Pariser-Parr (PP) and Mataga-Nishimoto (MN) potentials. In Fig. 1, the two kinds of Hückel screened potentials in benzene are shown, together with both the PP and MN bare potentials. The two kinds of Hückel screened potentials show quite a similar tendency in that, at small distances, the screening is strong and at large distances the anti-screening is appreciable.⁶⁾ Although both types of bare one-center potentials have the same value, the two kinds of one-center screened potentials are different from each other, since the one-center screened potential includes the contribution from other positions through the two-center potentials. For the other compounds treated in this paper, we calculate the Hückel and SCF screened potentials using only the MN potential, because the

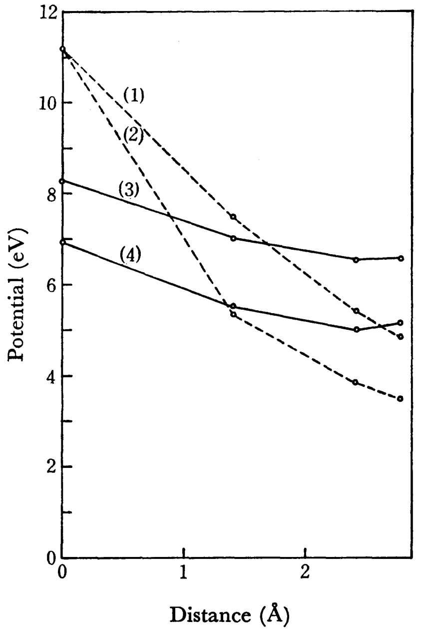


Fig. 1. Two kinds of the Hückel screened potentials in benzene obtained using the Pariser-Parr (PP) and Mataga-Nishimoto (MN) bare potentials; (1) the PP bare potential, (2) the MN bare potential, (3) the PP screened potential, (4) the MN screened potential.

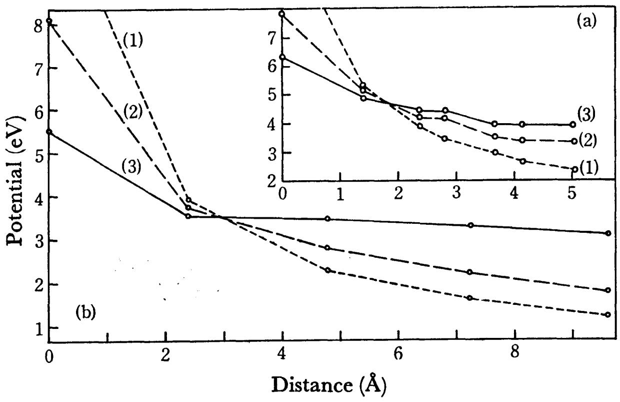


Fig. 2. The Hückel and SCF screened potentials in naphthalene (a) and in the polyene ($n=10$) (b); (1) the bare potential, (2) the SCF screened potential, (3) the Hückel screened potential.

---

5) C. Sandrofy, *Bull. Soc. Chim. France*, **1949**, 615.

6) It is considered that the anti-screening appeared in π-electron systems at large distances has to do with the finite size of the system.¹⁾

screened potentials obtained assuming the PP and MN potentials will probably show a similar qualitative behavior.

Difference between the Hückel and SCF Screened Potentials. The Hückel and SCF screened potentials in naphthalene and the polyene ($C_{10}H_{12}$) are illustrated in Fig. 2. The SCF screened potential shows a tendency similar to the Hückel screened potential, but it is intermediate between the Hückel screened and the bare potentials. That is, the effects of the screening and anti-screening in the SCF screened potential are both weakened. It seems that, in the Hückel screened potential, the effect of the screening and anti-screening of π-electrons tends to be overestimated.

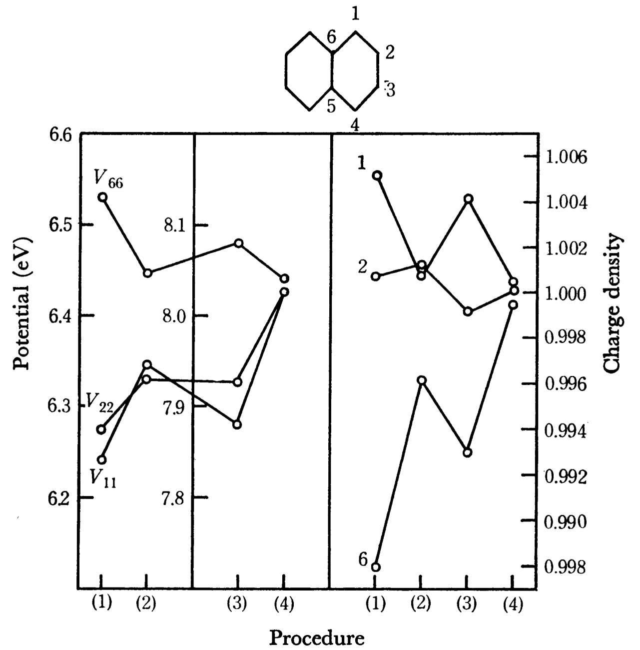


Fig. 3. The one-center screened potentials and charge densities in naphthalene calculated using the four procedures.

Figure 3 presents the one-center screened potentials and the charge densities in naphthalene calculated using the four procedures outlined above. It seems apparent that both the SCF procedure and the variable bond-length method have the effect of making the divergence among the calculated values small, and that this effect is stronger for the variable bond-length method than for the SCF procedure. As Procedure (4) involves both the SCF scheme and the variable bond-length method, the divergence becomes remarkably small. It may also be noted that such an effect appears for both the one-center screened potential and the charge density, and that the degree of breakdown of the Coulson-Rushbrooke theorem becomes appreciably small in the SCF state calculated using Procedure (4). In nonbenzenoid aromatic hydrocarbons and polyenes, there are no such definite effects.

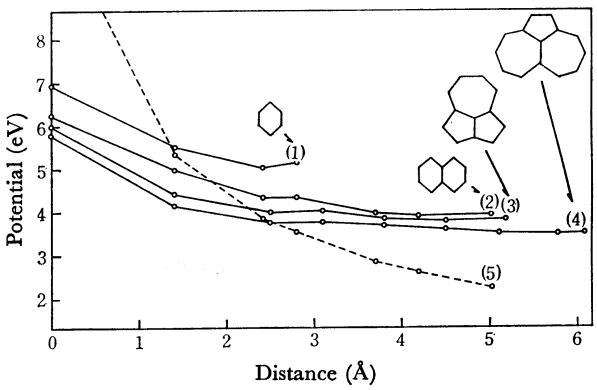


Fig. 4. The Hückel screened potentials; (1) benzene, (2) naphthalene, (3) aceazulylene, (4) aceheptylene, (5) the bare potential.

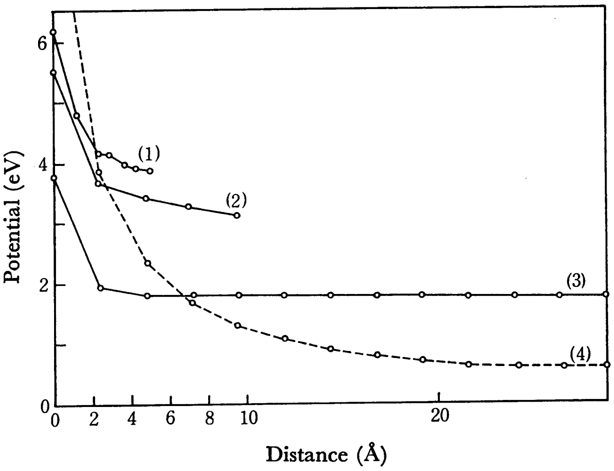


Fig. 5. The Hückel screened potentials in the polyenes ($n=10$ and 30); (1) naphthalene, (2) the polyene ($n=10$), (3) the polyene ($n=30$), (4) the bare potential.

Variation in the Hückel Screened Potential with Respect to the Sizes and Forms of the Molecules. The Hückel screened potentials in benzene, naphthalene, aceazulylene, and aceheptylene are presented in Fig. 4 and compared there with the bare potentials. In Fig. 5, the Hückel screened potentials in linear polyenes (the number of carbon atoms $n=10$ and 30) are shown and compared with the bare and the Hückel screened potentials in naphthalene ($n=10$). Since, in general, the effect of screening is different in various parts of molecules, there is a considerable divergence among the calculated screened potentials, in short ranges in particular; the average values are shown in these figures. From these figures, it will be seen that the screened potential in ring compounds decreases as the n increases, and that, when the n is the same, the screened potential is lower for the chain compound than for the ring compound. It may be stated generally that the larger or longer a molecule is, the stronger the screening in the short range and the weaker the anti-screening in the long range. In long linear polyenes, the Hückel screened potential tends to be constant even at small distances. In such a case, the atomic-orbital coefficients in molecular orbitals obtained from the SCF calculation using the Hückel screened potential tend to be the same as those of the Hückel orbitals.

Position Dependence of the Screened Potential in Polyenes and Benzenoid and Nonbenzenoid Aromatic Hydrocarbons. The carbon atoms in the polyene with $n=10$ are numbered as in Fig. 6. We divide the Hückel screened

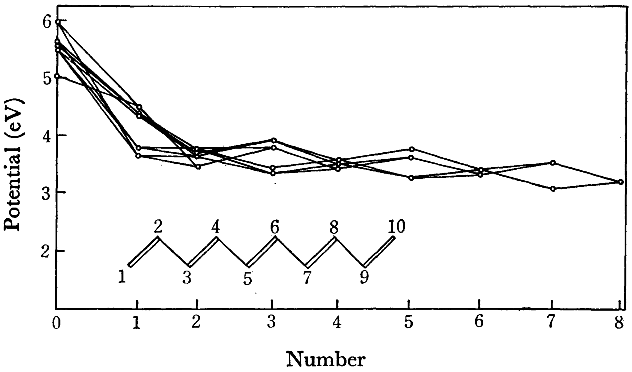


Fig. 6. The Hückel screened potentials in the polyene ($n=10$) plotted *versus* the number (for the meaning of the number, see the text).

potentials (Procedure (1)) into these groups: V_{11}, V_{12}, V_{13}, $\cdots$, $V_{1,10}$; V_{22}, V_{23}, $\cdots$, $V_{2,10}$; $\cdots$; V_{99}, $V_{9,10}$. In Fig. 6, the screened potentials in each group are plotted *versus* a number that indicates the kind of screened potential, that is, 0: one-center potentials V_{11}, V_{22}, V_{33}, $\cdots$; 1: the nearest two-center potentials V_{12}, V_{23}, V_{34}, $\cdots$; *etc.* Figure 6 shows that there are two kinds of numbers; that is, at an even number (including 0) one kind of screened potential exists, while at an odd number there exist two kinds of screened potentials in accordance with the strength of the screening.[7] The SCF screened potential (Procedure 3) in the polyene ($n=10$) presented in Fig. 7 shows a tendency similar to that in the Hückel screened potential.

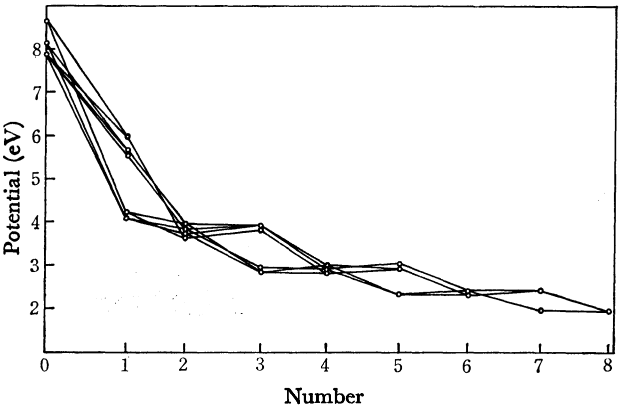


Fig. 7. The SCF screened potentials in the polyene ($n=10$) plotted *versus* the number (for the meaning of the number, see the text).

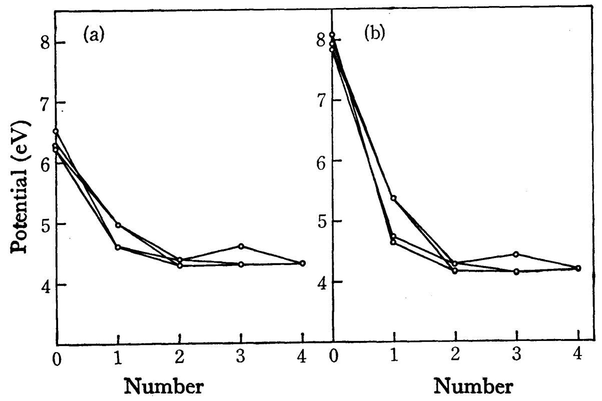


Fig. 8. The Hückel and SCF screened potentials in naphthalene plotted *versus* the number (for the meaning of the number, see the text); (a) the Hückel screened potential, (b) the SCF screened potential.

The results in naphthalene, azulene, aceazulylene, and aceheptylene are shown in Figs. 8—11 respectively. In naphthalene, the 5-membered ring in aceazulylene,

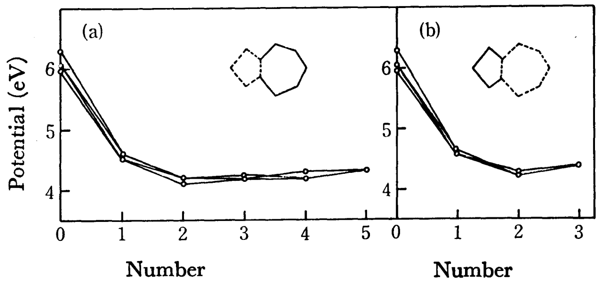


Fig. 9. The Hückel screened potentials in azulene plotted *versus* the number (for the meaning of the number, see the text); (a) the 7-membered ring, (b) the 5-membered ring.

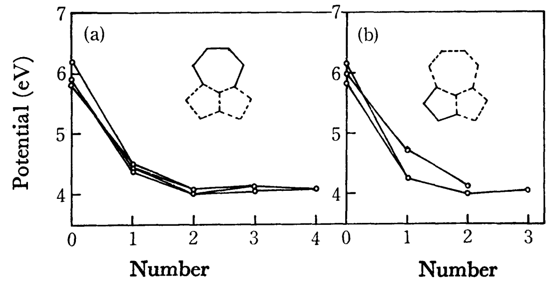


Fig. 10. The Hückel screened potentials in aceazulylene plotted *versus* the number (for the meaning of the number, see the text); (a) the 7-membered ring, (b) the 5-membered ring.

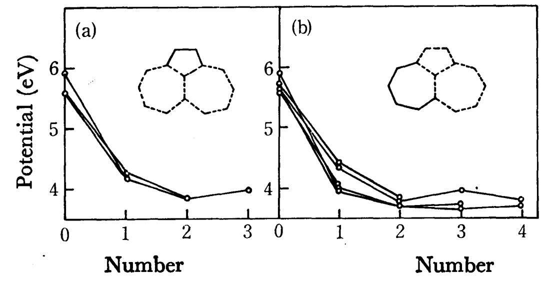


Fig. 11. The Hückel screened potentials in aceheptylene plotted *versus* the number (for the meaning of the number, see the text); (a) the 5-membered ring, (b) the 7-membered ring.

TABLE 1. EXCITATION ENERGIES (IN eV) OF BENZENE

	Symmetry	HSP[a]	BP[b]	Exp.[8]
Singlet	B_{2u}	4.86	4.90	4.89
	B_{1u}	6.08	6.19	6.14
Triplet	B_{1u}	3.69	2.48	3.66
	E_{1u}	4.60	3.99	4.69

a) HSP: the Hückel screened potential.
b) BP: the bare potential.

---

7) At odd number i, one kind of the screened potentials consists of the potentials between the $2j$-th carbon atoms and the $(2j+i)$-th carbon atoms, and the other consists of the potentials between the $(2j+1)$-th carbon atoms and the $(2j+1+i)$th carbon atoms.

8) D. R. Kearns, *J. Chem. Phys.*, **36**, 1608 (1960).

TABLE 2. EXCITATION ENERGIES (IN eV) OF NAPHTHALENE

	Symmetry	HSP	Variable			Exp.
			BP	HSP	SCFSP[a]	
Singlet	B_{3u}	4.08	4.18	4.15	4.43	3.97,[9] 4.11[10]
	B_{2u}	4.31	4.68	4.41	4.97	4.51,[9] 4.61[10]
Triplet	B_{2u}	2.44	1.87	2.67	2.88	2.61
	B_{1g}	3.30	2.92	3.40	3.57	

a) SCFSP: the SCF screened potential.

TABLE 3. EXCITATION ENERGIES (IN eV) OF ACEAZULYLENE

	Symmetry	HSP	Variable		Exp.[a]
			BP[11]	HSP	
Singlet	B_2	1.68	1.73	1.95	1.84
	A_1	2.92	2.91	3.00	2.59, 2.76, 2.94
	B_2	3.64	3.86	3.41	3.19, 3.25, 3.37
	A_1	3.70	3.64	3.69	3.66, 3.79, 3.97
	B_2	4.35	4.79	4.74	4.63
Triplet	B_2	1.90	1.40	1.90	
	A_1	3.20	1.58	2.16	

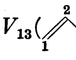
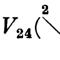
a) The absorption spectra of dimethyl derivatives.[12]

and the 7-membered ring in aceheptylene, a tendency similar to that in the polyene appears, while in azulene, the 7-membered ring in aceazulylene, and the 5-membered ring in aceheptylene, at each of the numbers the various screened potentials have almost the same value.

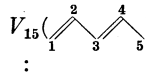
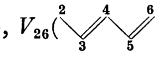
We can understand the above characteristics of the screened potential as follows. In the polyene ($n=10$), the screened potentials can be divided into the following two groups according to the numbers:

one group: even numbers (including 0)

0: V_{11}, V_{22}, V_{33}, $\cdots$

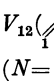
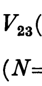
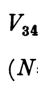
2: V_{13}(
), V_{24}(
), $\cdots$

(The number of double bonds $N=1$)

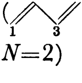
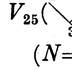
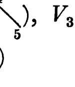
4: V_{15}(
), V_{26}(
), $\cdots$ ($N=2$)

⋮

the other group: odd numbers

1: V_{12}(
), V_{23}(
), V_{34}(
), $\cdots$

($N=1$) ($N=0$) ($N=1$)

3: V_{14}(
), V_{25}(
), V_{36}(
), $\cdots$

($N=2$) ($N=1$) ($N=2$)

⋮

From the above classification of the screened potentials, it may be seen that there are two kinds of screening at the odd numbers in molecules such as polyene in which there exists a strong bond alternation, while there is only one kind of screening at the odd numbers in molecules which do not show a clear bond alternation—for example, benzene and azulene. In naphthalene, there is a fairly clear double-bond fixation, so that the characteristics of the screened potential in Fig. 8 are the same as those of the polyene.

TABLE 4. EXCITATION ENERGIES (IN eV) OF ACEHEPTYLENE

	Symmetry	HSP	Variable		Exp.[a]
			BP[11]	HSP	
Singlet	B_2	1.50	1.52	1.77	1.55
	A_1	2.79	2.89	2.78	2.72
	B_2	3.34	3.47	3.10	3.20
	A_1	3.48	3.82	3.80	3.96, 4.16
	B_2	3.96	4.48	4.27	4.35, 4.56
Triplet	B_2	1.70	1.15	1.57	
	B_2	3.13	1.40	2.01	

a) The absorption spectra of dimethyl derivatives.[12]

Transition Energies of Benzene, Naphthalene, Aceazulylene, and Aceheptylene. Tables 1—4 show the transition energies calculated by using the modified CI method assuming the Hückel screened potential and the SCF screened potential, together with those calculated assuming the bare potential. In these tables, "variable" means that a calculation has been performed in combination with the variable bond-length SCF method. The results agree well with the experimental values. It may be noted that triplet excitation energies calculated using the screened potential are in better agreement with the experimental values than those calculated using the bare potential.

This research was supported in part by a grant from Takeda Sciense Foundation.

---

9) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London (1963).

10) American Petroleum Institute, Research Project 44. Ultraviolet Absorption Spectral Data. Carnegie Institute of Thcenology.

11) H. Yamaguchi, T. Terasaka, and T. Nakajima, *Theoret. Chim. Acta* (Berl.), **18**, 255 (1970).

12) K. Hafner and J. Schneider, *Angew. Chem.*, **70**, 702 (1958); *Ann. Chem.*, **624**, 37 (1959); K. Hafner, personal communication to T. Nakajima.