Calculations of the Energy Levels of Cycloöctatetraene (C_8H_8)

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1. Introduction

The cycloöctatetraene molecule has already been treated by Hückel(1) according to the molecular orbital method. But as its molecular structure was not known at the time, he treated its molecule as plane and suggested the possibility of its substance to be paramagnetic.

Lately, by R. C Pink and A. R. Ubbelohde(2) and also by the members of our laboratory(3) it is found experimentally that the substance is not paramagnetic but diamagnetic* like many other organic substances and also that its molecule has no resultant spin in the ground state. The purpose of the present paper is to calculate the energy levels of the molecule from the stand-point of the Heitler-London-Slater-Pauling method,(4)(5)(6) assuming different structures (D_{2d} and D_{4d}) proposed by different investigators and from different experimental grounds, and also to show which structure is in better agreement with the experimental results of magnetic susceptibility, absorption spectra and thermochemical data.

The structure of cycloöctatetraene, though investigated by several physico-chemical methods, but has not yet been decided. Until now, as a result of investigation, the structures of C_8H_8, "Crown Form"(7)(8)(9) (D_4, or D_{4d}) and "Tub Form" (D_{2d})(10)(11)(12) are reported. (Fig. 1).

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* The molar magnetic susceptibility was found in our laboratory to be -55.3×10^{-6}, independent of the temperature between 20° and 80°.

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(2) R. C. Pink and A. R. Ubbelohde, *Nature*, **160**, 502 (1947); *Trans. Faraday Soc.*, **44**, 708–16 (1948); *Chem. Abst.*, No. 7 (Apr. 10), (1949).

(3) S. Shida and S. Fujii, Scientific Meeting of Tokyo Institute of Technology (August 1949).

(4) J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

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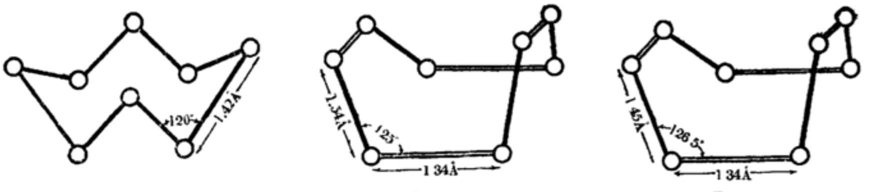

D_{4d} (Gas phase by the method of electron diffraction(7)) D_{2d} (Solid phase by the method of X-ray diffraction(10)(11)) D_{2d} (Gas phase by the method of electron diffraction(12))

Fig. 1.

First, in calculating the energy levels of C_8H_8 as the symmetry of D_{2d}, a molecule of C_8H_8 is treated as follows: Each carbon atom has one π-electron whose density cloud is a dumbbell with its axis perpendicular to the plane of the σ-bonds (approximately sp^2-bonds). It is assumed that the interaction of the π-electron and the σ-electron is small.

2. Calculation of Singlet States

All the possible structures will be described first. They are linearly independent, namely, the canonical sets for cycloöctatetraene; the two Kekule structures (Ψ^1, Ψ^2), the eight Dewar I structures (Ψ^3, Ψ^5, ..., Ψ^{10}) and the four Dewar II structures (Ψ^{11}, Ψ^{12}, Ψ^{13}, Ψ^{14}) exist. These are shown in Fig. 2. For instance, two Kekule structures for benzene have identical energy, but those for cycloöctatetraene (D_{2d}) have not. This arises from the fact that the exchange integral is devided into two.

$\Psi^k(k=1, 2, 3, \ldots, 14)$, wave function attached to the each structure k of the canonical set, is

$$\Psi^k=\frac{1}{2^4(8!)^{\frac{1}{2}}}\sum_p(-1)^p P\psi_1(1)\psi_2(2)(\alpha_1\beta_2-\beta_1\alpha_2) \times\psi_3(3)\psi_4(4)(\alpha_3\beta_4-\beta_3\alpha_4)\times \quad \ldots.(1)$$

The energy levels are given by solving the secular equation

$$\det\|\Psi^j\,|\,H-W\,|\,\Psi^k\|=0 \quad \ldots.(2)$$

$$(\Psi^j\,|\,H-W\,|\,\Psi^k)=U_{jk}(Q-W)+V_{jk}\alpha+W_{jk}\alpha' \quad \ldots.(3)$$

$$Q=\int\psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)\psi_7(7) \psi_8(8)H\tilde{\psi}_1(1)\tilde{\psi}_2(2)\tilde{\psi}_3(3)\tilde{\psi}_4(4)\tilde{\psi}_5(5)\tilde{\psi}_6(6) \tilde{\psi}_7(7)\tilde{\psi}_8(8)d\tau \quad \ldots.(4)$$

$$\alpha=\int\psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)\psi_7(7) \psi_8(8)H\tilde{\psi}_1(2)\tilde{\psi}_2(1)\tilde{\psi}_3(3)\tilde{\psi}_4(4)\tilde{\psi}_5(5)\tilde{\psi}_6(6) \tilde{\psi}_7(7)\tilde{\psi}_8(8)d\tau \quad \ldots.(5)$$

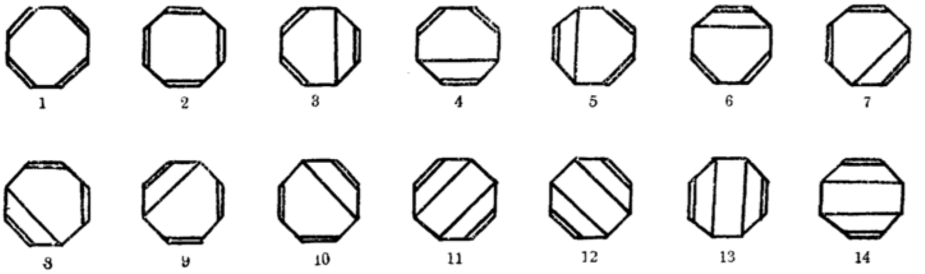

Fig. 2.—1~2, Kekule structures; 3~10, Dewar I structures; 11~14, Dewar II structures.

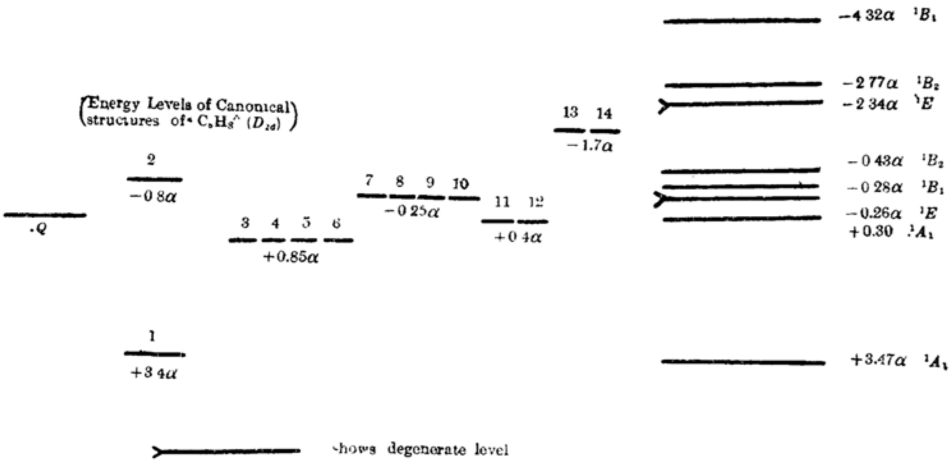

Fig. 3.—Energy levels of singlet states except four $^1A_1$ levels (in the case of $\alpha'=0.3\alpha$).

Table 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	$^{8}/(32\alpha-16\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(16\alpha-2\alpha')$	$^{4}/(16\alpha-2\alpha')$	$^{4}/(16\alpha-2\alpha')$	$^{4}/(16\alpha-2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{4}/(16\alpha-8\alpha')$	$^{4}/(16\alpha-8\alpha'$	$^{2}/8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$
2	$^{1}/(4\alpha+4\alpha')$	$^{8}/(32\alpha'-16\alpha)$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{4}/(16\alpha'-2\alpha)$	$^{4}/(16\alpha'-2\alpha)$	$^{4}/(16\alpha'-2\alpha)$	$^{4}/(16\alpha'-2\alpha)$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{4}/(16\alpha'-8\alpha)$	$^{4}/(16\alpha'-8\alpha)$
3	$^{4}/(16\alpha-2\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{8}/(8\alpha-4\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$
4	$^{4}/(16\alpha-2\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{8}/(8\alpha-4\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$
5	$^{4}/(16\alpha-2\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{8}/(8\alpha-4\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$
6	$^{4}/(16\alpha-2\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{8}/(8\alpha-4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$
7	$^{2}/(8\alpha+2\alpha')$	$^{4}/(16\alpha'-2\alpha)$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{8}/(8\alpha'-4\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$
8	$^{2}/(8\alpha+2\alpha')$	$^{4}/(16\alpha'-2\alpha)$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{8}/(8\alpha'-4\alpha)$	$2/(^{8}\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$
9	$^{2}/(8\alpha+2\alpha')$	$^{4}/(16\alpha'-2\alpha)$	$^{4}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{8}/(8\alpha'-4\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$
10	$^{2}/(8\alpha+2\alpha')$	$^{4}/(16\alpha'-2\alpha)$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{8}/(8\alpha'-4\alpha)$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$
11	$^{4}/(16\alpha-8\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{8}/(8\alpha-16\alpha')$	$^{2}/(8\alpha-4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$
12	$^{4}/(16\alpha-8\alpha')$	$^{2}/(2\alpha+8\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{2}/(8\alpha+2\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{2}/(8\alpha-4\alpha')$	$^{8}/(8\alpha-16\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$
13	$^{2}/(8\alpha+2\alpha')$	$^{4}/(16\alpha'-8\alpha)$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{8}/(8\alpha'-16\alpha)$	$^{2}/(8\alpha'-4\alpha)$
14	$^{2}/(8\alpha+2\alpha')$	$^{4}/(16\alpha'-8\alpha)$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{4}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{2}/(8\alpha'+2\alpha)$	$^{1}/(4\alpha+4\alpha')$	$^{1}/(4\alpha+4\alpha')$	$^{2}/(8\alpha'-4\alpha)$	$^{8}/(8\alpha'-16\alpha)$

Notation $^{8}/_{32\alpha-16\alpha'}=8(Q-W)+(32\alpha-16\alpha')$

$$\alpha'=\int\psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)\psi_7(7)\psi_8(8)H\tilde{\psi}_1(1)\tilde{\psi}_2(3)\tilde{\psi}_3(2)\tilde{\psi}_4(4)\tilde{\psi}_5(5)\tilde{\psi}_6(6)\tilde{\psi}_7(7)\tilde{\psi}_8(8) \qquad \ldots.(6)$$

U_{jk}, V_{jk}, W_{jk} is determined by Pauling's island method.

Then the Kekule I structure has an energy lowering of $(4\alpha-2\alpha')$, whereas the Kekule II structure has an energy lowering of $(4\alpha'-2\alpha)$. The Kekule II structure has a higher energy than the Kekule I structure $\alpha'<\alpha$ as explained in Section 5.

The determinant evaluated for cyloöctatetraene (fourteen canonical structures) is shown in Table 1.

Factorizing the secular determinant by a linear combination of the canonical structures, the energy levels of the singlet states of C_8H_8 (D_{2d}) are obtained.

In the next problem, the symmetry of the levels may be found by the group theory.

3. Selection Rules

The symmetry of the fourteen levels may be found from the characters of the reducible representation on the basis of the fourteen structures.

If the symmetry of C_8H_8 is D_{2d}, its character is as shown in Table 2.

Table 2

$V_d=D_{2d}$	E	C_2	$2iC_4=2S_4$	$2C'_2$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	1	−1	1	−1
$B_2(z)$	1	1	−1	−1	1
$E(x\pm iy)$	2	−2	0	0	0

The characters of the symmetry operations in the reducible representation Γ for C_8H_8 are shown in Table 3.

Table 3

	E	C_2	$2iC_4=2S_4$	$2C'_2$	$2\sigma_d$
Γ	14	6	2	6	6

The reducible representation Γ is broken into its irreducible parts $\Gamma=\sum_j a_i\Gamma_j$ by means of the character tables (Tables 2 and 3), namely

$$\Gamma=6A_1+2B_1+2B_2+2E \qquad \ldots.(7)$$

These irreducible repesentations correspond to the fourteen energy levels of singlet state. The selection rule for transitions between $^1A_1$ and all the other energy levels will be discussed by the group theory.

$$\begin{cases} P_z & A_1B_2A_1,\ A_1B_2B_1,\ A_1B_2E \\ P_{x,y} & A_1EA_1,\ \ A_1EB_1,\ \ A_1EB_2 \end{cases}$$

The transitions from ground state to the excited levels are forbidden for reduced form does not contain A_1.

$$\begin{cases} P_z & A_1B_2B_2=A_1 \\ P_{x,y} & A_1E\,E=A_1+A_2+B_1+B_2 \end{cases}$$

The transitions from ground state to the B_2, E levels are allowed.

The transitions from $^1A_1$ to $^1B_2$ and ^1E are allowed. In this point C_8H_8 is different from benzene for the transition from the ground state of benzene to the excited state is forbidden so far as the polar terms are neglected. In the following chapter the result of calculation, by which the singlet ground state was found out to be more stable than the triplet ground state, will be described.

4. Calculation of Triplet States

The triplet states of cycloöctatetraene are calculated by analogous method to that in the case of the singlet states.

The canonical set is composed of twenty eight structures. But the energy of triplet ground state is approximately the lowest of those, calculated from the only eight canonical structures in the case of D_{2d}, because the remaining twenty canonical structures have higher energies than the former.

The eight canonical structures are shown in Fig. 4 and the secular determinant is given in Table 4.

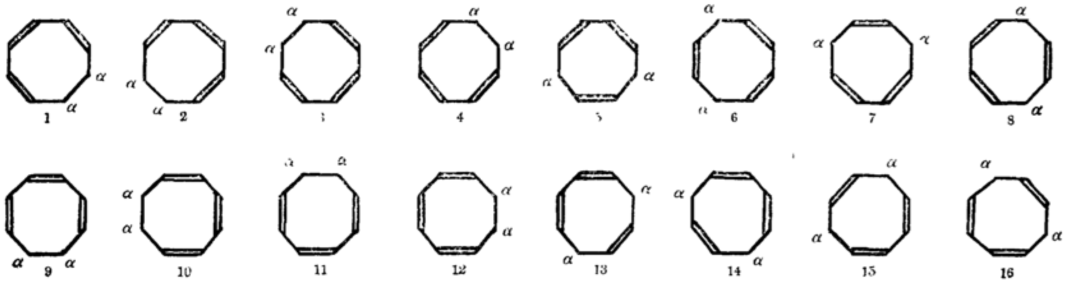

Fig. 4.—Upper eight canonical structures are used for the triplet states of D_{2d} and all of sixteen canonical structures for the triplet states of D_{4d}.

Table 4

	1	2	3	4	5	6	7	8
1	$8/16\alpha-16\alpha'$	$0/4\alpha'$	$0/0$	$0/4\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$
2	$0/4\alpha'$	$8/16\alpha-16\alpha'$	$0/4\alpha'$	$0/0$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$
3	$0/0$	$0/4\alpha'$	$8/16\alpha-16\alpha'$	$0/4\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$
4	$0/4\alpha'$	$0/0$	$0/4\alpha'$	$8/16\alpha-16\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$
5	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$8/8\alpha-4\alpha'$	$2/4\alpha+2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$
6	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$	$8/8\alpha-4\alpha'$	$2/4\alpha+2\alpha'$	$0/2\alpha'$
7	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$	$8/8\alpha-4\alpha'$	$2/4\alpha+2\alpha'$
8	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$2/4\alpha+2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$	$8/8\alpha-4\alpha'$

The secular determinant is factorized by linear combination of eight canonical structures like the singlet states. The same parameter, α, appeared as it did in the energy of the singlet states. The energy of the triplet ground state calculated is -1.84α (if $\alpha'=0.2\alpha$) or -1.76α (if $\alpha'=0.3\alpha$). Therefore, it is expected from the H-L-S-P method that C_8H_8 is diamagnetic.*

5. Energy Levels and Resonance Energy

The energy levels of singlet states of C_8H_8, except four $^1A_1$ levels in each case of $\alpha'=0.2\alpha$, 0.25α, 0.3α, 0.35α, are given in Table 5. The reason why the values of α' are selected as above will be shown in section 7

The two Kekule structures have not the same energy and the higher Kekule structure scarcely affects the ground state. Then the lower Kekule structure, the four lower Dewar I structures and the two lower Dewer II structures greatly contribute to the energy of the ground state.

In order to determine the value of the splitting up of the energy levels, it is necessary to find the numerical values of α, α'. The two methods of finding these values are as follows: first, experimentally from thermochemical data, secondly, theoretically by the $2p\pi$ hydrogen-like functions.

Table 5

The Energy Levels of Singlet States of C_8H_8 Except Four $^1A_1$ Levels.

	$\alpha'=0.2\alpha$	$\alpha'=0.25$	$\alpha'=0.3\alpha$	$\alpha'=0.35\alpha$
$^1B_1$	-4.21α	-4.27α	-4.32α	-4.38α
$^1B_2$	-2.48α	-2.62α	-2.77α	-2.92α
^1E	-2.22α	-2.28α	-2.34α	-2.41α
$^1B_2$	-0.32α	-0.38α	-0.43α	-0.48α
$^1B_1$	-0.19α	-0.23α	-0.28α	-0.32α
^1E	-0.18α	-0.22α	-0.26α	-0.29α
$^1A_1$	0.10α	0.20α	0.30α	0.40α
$^1A_1$	3.63α	3.55α	3.47α	3.40α

The heat of formation is calculated from recent data.⁽¹³⁾

$$8C+8H=C_8H_8+1354.8\text{ kcal.}$$

The values of bond energy obtained from recent data⁽¹⁴⁾ are as follows:

$$\left.\begin{array}{l}\text{C-C}=\ 60.3\text{ kcal.}\\ \text{C-C}=102.9\text{ kcal.}\\ \text{C-H}=\ 87.15\text{ kcal.}\end{array}\right\}\longrightarrow\left\{\begin{array}{l}\text{therefore the heat}\\ \text{of formation of}\\ C_8H_8=1350\text{ kcal.}\end{array}\right.$$

This difference, 4.8 kcal, may be taken as the experimental resonance energy which is about 11%∼13% of that for benzene. (Benzene, $\alpha=-1.55$⁽¹⁵⁾ or -1.92 e.V.⁽¹⁶⁾)

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* The results calculated by the G-M-S method also suggest us that $C_8H_8(D_{2d})$ is diamagnetic. This calculation will be publisded.

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But it is necessary to examine critically the resonance energy of this experimental data. The structure of C_8H_8 is not plane, therefore, the steric hindrance demands considerations. Namely, the steric influences between CH and CH, and that of the bond energy of C=C must be taken into considerations.

Next we shall calculate by the $2p\pi$ hydrogen-like functions. The structure of cycloöctatetraene proposed by Hedberg and Schomaker(12) is as follows:

$$\angle CCC = 126.5^\circ \quad C=C=1.34\ \text{Å}. \quad C-C=1.45\ \text{Å}.$$

The eigenfunctions are:

$$\Psi_\pi(r,\theta,\varphi)=\sqrt{\frac{Z^5}{32\pi}}\,e^{-Z\,r/2}\,r\sin\theta\cos\varphi\,..\,(8)$$

The effective nuclear charge Z was chosen to be $Z=3.18$, a value which was obtained by Zener.(17)

Although Griffing(18) calculated the value of α for benzene, it was known that this approximate calculation would not give the correct absolute value. Then, the value of α' is calculated on the assumption that the exchange integral depends on the overlap of $2p\pi$ function, as this value depends on approximately the angle between $2p\pi$ functions at the neighboring carbon nuclei and $\alpha'=0.3\alpha$ is obtained. Then energy levels are calculated using various value of $\alpha'(0.20\alpha, 0.25\alpha, 0.30\alpha, 0.35\alpha)$. The resonance energy is calculated by use of $\alpha=1.5$ e.V. This value of α is obtained with regard to the exchange integral of benzene and the effect of geometrical form of cycloöctatetraene upon the strength of binding in comparison with that of benzene. But the exact value of α must be obtained in future from the detailed experimental data.

Table 6

	$\alpha'=$ 0.2α	$\alpha'=$ 0.25α	$\alpha'=$ 0.30α	$\alpha'=$ 0.35α
Ground state	3.63α	3.55α	3.47α	3.40α
Kekule I	3.60α	3.50α	3.40α	3.30α
Resonace energy	0.03α 1.04 kcal.	0.05α 1.73 kcal.	0.07α 2.42 kcal.	0.10α 3.46 kcal.

The larger the exchange integral α', the larger the resonance energy grows, as mentioned above.

6. Absorption Spectrum

The absorption spectrum of cycloöctatetraene(19) is shown in Fig. 5.

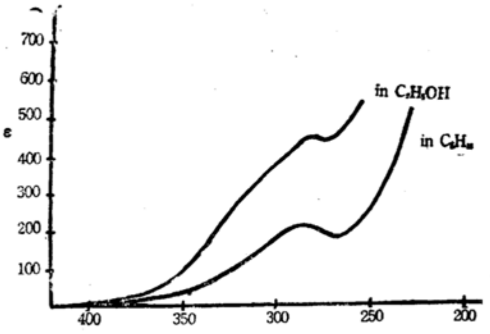

Fig. 5.

In our judgment about the value of ε, the shoulder of the absorption band 2800 Å. is the forbidden transition. Hence this absorption band may be the $^1A_1 \rightarrow {}^1A_1$ transition calculated by the H-L-S-P method.* The absorption band below 2000Å. which is now investigated, is supposed to be the allowed transition $^1A_1 \rightarrow {}^1E$. The wave lengths of each transition calculated by the H-L-S-P method is shown in Table 7.

Table 7

	$\alpha'=$ 0.2α	$\alpha'=$ 0.25α	$\alpha'=$ 0.30α	$\alpha'=$ 0.35α
$^1A_1 \rightarrow {}^1A_1$	3.53α	3.35α	3.17α	3.00α
Wave length	2330Å.	2460Å.	2600Å.	2740Å.
$^1A_1 \rightarrow {}^1E$	3.81α	3.77α	3.73α	3.69α
Wave length	2160Å.	2180Å.	2210Å.	2230Å.

7. In the Case of D_{4d}

The experimental results that the structure of cycloöctatetraene may be "Crown Form" (D_{4d}) are reported by O. Bastiaisen, O. Hassel and A. Langseth(7) (electron diffraction), and so the energy levels of C_8H_8 is calculated to have the symmetry of D_{4d} by the H-L-S-P method. The procedure of calculation is similar to that in the case of D_{2d}.

In the symmetry D_{2d} there are two different exchange integrals α and α', but in D_{4d} $\alpha=\alpha'$, so the energies of two Kekule structures are identical. Then the determinant of C_8H_8 (D_{4d}) is obtained by putting $\alpha=\alpha'$ in the determinant of D_{2d}. The energy levels of singlet states of C_8H_8 (D_{4d}) are obtained after calculating the above determinant, and the symmetry of the levels is decided from the group theory, and the transition only from $^1A_1$ to the symmetry $^1E_1$ is allowed. The results are shown in Fig. 9.

For the purpose of obtaining the energy of the triplet ground state the calculation is made using sixteen canonical structures, excepting

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(17) C. Zener, *Phys. Rev.*, **36**, 51 (1930).

(18) V. Griffing, *J. Chem. Phys.*, **15**, 421 (1947).

(19) S. Miyakawa, unpublished.

* We obtain that $^1A_2$ level is lower than $^1A_1$ level calculating by the G-M-S method, and the calculation by the H-L-S-P method including polar terms produces $^1A_2$ level, where the value of $^1A_2$ level cannot be calculated because the new Coulomb integral and exchange integral are not known exactly. So we cannot decide whether 2800Å. band is the $^1A_1 \rightarrow {}^1A_1$ transition or the $^1A_1 \rightarrow {}^1A_2$ transition.

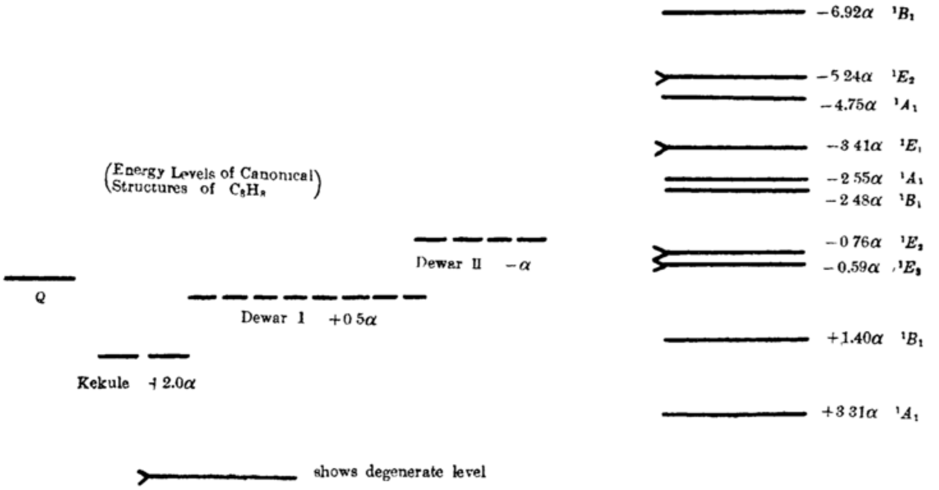

Fig. 6.—Energy levels of singlet states in the case of D_{4d}.

the twelve structures which have higher energies in twenty eight structures, and get 2.24α as the energy of the triplet ground state. The energy of the singlet ground state (3.31α) is lower than that of the triplet ground state (2.24α). The singlet state $^1A_1$ is, therefore, the ground state of cycloöctatetraene, and it is expected to be diamagnetic from the standpoint of the H-L-S-P method.

The resonance energy for C_8H_8 (D_{4d}) is as following. The singlet ground state ($^1A_1$) has the energy 3.31α, (Fig. 6) whereas one Kekule structure which is the structure of the lowest energy, has an energy of 2.0α. The difference, 1.31α, between the energy of the ground state and that of the Kekule structure is resonance energy.(20) The resonance energy for C_8H_8 is experimentally 4.8 kcal. (§ 5), then $1.31\alpha = 4.8$ kcal., and we obtain $\alpha = 3.66$ kcal. And, theoretically, the values of α in each case of various angles between carbons are calculated, on the assumption that the Hamiltonian of C_8H_8 is approximately the same as that C_6H_6 and the exchange integral depends on the overlap of $2p\pi$ function as this value depends on approximately the angle between $2p\pi$ functions at the neighboring carbon nuclei (Table 8). The value of α which is calculated from the absorption spectrum is different from that obtained from the thermochemical data and the numerical calculation. If the structure of cycloöctatetraene is D_{4d}, ∠CCC angle may be greater than 120°(8), because in case of 120° the resonance energy is so small that cycloöctatetraene cannot exist stable. ∠CCC of cycloöctatatetraene forms the angle that is unstabilized by the steric hindrance and stabilized by the resonance energy balance.

Table 8

∠CCC	$2p\pi \sim 2p\pi$ angle	α	
		e. V.	kcal.
120°	80°	-5.31×10^{-2}	-1.22
121°	78°	-7.61×10^{-2}	-1.75
122°	75.8°	-1.06×10^{-1}	-2.44
123°	73.4°	-1.45×10^{-1}	-3.34
124°	71.5°	-1.77×10^{-1}	-4.08
125°	68°	-2.48×10^{-1}	-5.72
126°	65°	-3.17×10^{-1}	-7.31
127°	61.2°	-3.68×10^{-1}	-8.48
128°	58.3°	-4.89×10^{-1}	-11.27

So far the interaction only between neighboring atoms has been considered. But if cycloöctatetraene is D_{4d} and α is small, the interaction between the second neighboring atoms is not neglected. In respect to this point a further investigation is going on.

Summary

The energy levels of cycloöctatetraene as D_{2d} and D_{4d} were calculated by the H-L-S-P method. Then we showed that the ground state of C_8H_8 (D_{2d} and D_{4d}) may be diamagnetic. The resonance energy of C_8H_8 (D_{2d} and D_{4d}) is about several kilocalories (about ten per cent of that of benzene) from thermochemical data and numerical calculation. The wave length of absorption spectra calculated assuming D_{2d} is in better agreement with the experimental result than that calculated assuming D_{4d}.

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(20) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934). Resonance Energy $= 1.29\alpha$.