

very little affected by the severe thermal pretreatments of the catalyst which were employed. Since there is little *a priori* reason to expect this, the results are of particular interest. The importance of applying a method such as that described in this paper to study

the factors influencing the catalytic activities of supported metals cannot be overemphasized.

**Acknowledgment.**—The authors gratefully acknowledge the contributions of Messrs. R. C. Parker and E. M. Kelley in the performance of the experiments.

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## The Acetylacetonate Anion. Molecular Orbital Calculations in the Huckel and Self-Consistent Field Approximations<sup>1</sup>

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RECEIVED FEBRUARY 7, 1964

Huckel and self-consistent field calculations of the acetylacetonate ion  $\pi$ -electron structure have been made. In contrast to the marked sensitivity of the Hückel results to the parameter choice, the s.c.f. results are relatively independent of these quantities. The effects of metal ion charge and penetration integrals largely cancel out, and a simplified s.c.f. treatment is adequate for the calculation of transition energies and intensities.

### Introduction

In the interpretation of the spectra of metal complexes, it is often useful to distinguish electronic transitions largely localized within the ligands from those involving charge transfer between the metal ion and ligands. The spectra of metal complexes in which the acetylacetonate ion is the ligand have been studied in detail,<sup>2,3</sup> and attempts to distinguish ligand-localized from charge-transfer transitions have been made.<sup>3-6</sup> Such an analysis generally proceeds by first examining the spectrum of the free ligand and then considering the perturbing effect of the metal ion on the ligand states. The electronic structure of the acetylacetonate anion has been calculated by two semiempirical procedures—the Hückel<sup>3,4</sup> and self-consistent field (s.c.f.) methods.<sup>6</sup>

The success of the Hückel method in the interpretation of the spectra of alternant hydrocarbons coupled with the computational simplicity of this scheme has led to its extensive applications to  $\pi$ -electron systems. The widespread availability of digital computers has now minimized the computational advantages of the Hückel method. In this paper, the electronic structures of the acetylacetonate ion as determined by the Hückel method and a computationally simple version of the s.c.f. method are compared in order to determine the relative merits of each technique.

The determination of the electronic structures of metal acetylacetonates with two and three ligands should be based on a knowledge of the single ligand structure. In this study, the first step in the treatment of the more general problem, the acetylacetonate ion (as in alkali metal complexes), is considered.

**Hückel Calculations.**<sup>7</sup>—In the Hückel method, the normalized molecular orbitals are of the LCAO form

$$\phi_i = \sum_p c_{ip} \chi_p \quad (1)$$

- (1) Supported by the United States Atomic Energy Commission.  
 (2) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).  
 (3) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).  
 (4) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97, 102 (1963).  
 (5) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962).  
 (6) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963).  
 (7) For a comprehensive survey of this method see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

where the summation index  $p$  extends over all the atoms in the  $\pi$ -electron framework or "core." Neglecting overlap, the coefficients,  $c_{ip}$ , and orbital energies,  $\epsilon_i$ , are determined by diagonalizing the  $\mathbf{H}$  matrix, with elements defined as

$$H_{pq} = \int \chi_p H^{\text{eff}} \chi_q d\tau$$

The Coulomb integrals,  $H_{pp} \equiv \alpha_p$ , and the resonance integrals,  $H_{pq} \equiv \beta_{pq}$  (these are assumed to be zero unless  $p$  and  $q$  refer to neighboring atoms), are assigned semiempirically, and the  $\mathbf{H}$  matrix may be diagonalized with a digital computer using a program in which the  $c_{ip}$  and  $\epsilon_i$  are evaluated.

In the simple Hückel method, electron repulsion is not incorporated explicitly, but is included to some extent by the choice of  $\alpha_p$  and  $\beta_{pq}$  parameters. This procedure has been fairly successful in treating the spectra of alternant hydrocarbons, but serious ambiguities arise when heteroatoms are included in the  $\pi$ -electron system.<sup>8,9</sup> The  $\alpha_p$  parameters must then be adjusted for the differential electronegativity of the atoms and the  $\beta_{pq}$  altered for the varying bond lengths. The uncertainties inherent in this approach can be seen by reference to Table I where the results of the three Hückel calculations are summarized. The numbering system is shown in Fig. 1. In calculation Ia,

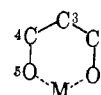


Figure 1.

parameters rather similar to those suggested by Streitwieser<sup>7</sup> were employed. The effect of the metal ion in increasing the electronegativity of the oxygen atoms was intentionally overestimated in calculation Ib, while in calculation Ic another "reasonable" choice of parameters was employed.<sup>10</sup> The six  $\pi$ -electrons fill the three lowest orbitals,  $\phi_1$ – $\phi_3$ , and in all three cases the lowest energy transition is assigned as  $\phi_3 \rightarrow \phi_4$ . The assignment of the next higher transition is doubtful, however. Not only are the transition energies

- (8) M. J. S. Dewar, *Rev. Mod. Phys.*, **35**, 586 (1963).  
 (9) G. Del Re and R. G. Parr, *ibid.*, **35**, 604 (1963).  
 (10) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961), and private communication.

TABLE I  
 HUCKEL RESULTS<sup>a</sup>

Parameters, e.v.	Ia	Ib	Ic
$\alpha_1$	-2.74	-5.48	-1.67
$\alpha_2$	+0.27	0	-0.16
$\alpha_3$	0	0	0
$\beta_{12}$	-2.46	-2.74	-4.08
$\beta_{23}$	-2.74	-2.74	-2.74
Transition energies, e.v.			
$\phi_3 \rightarrow \phi_4$	3.44	3.87	4.01
$\phi_3 \rightarrow \phi_5$	6.26	7.02	5.95
$\phi_2 \rightarrow \phi_4$	5.78	7.75	8.29
Charge densities			
$P_{11}$	1.698	1.812	1.406
$P_{22}$	0.704	0.620	0.887
$P_{33}$	1.196	1.136	1.414

<sup>a</sup> Calculation Ia parameters are similar to those recommended by Streitwieser<sup>7</sup>; calculation Ib parameters are overcorrected for metal ion charge; calculation Ic parameters are those employed by Barnum.<sup>10</sup> In all three cases  $\beta_{C-C} = -2.74$  e.v., and  $\alpha_3 = 0$  was chosen as the reference energy.

dependent upon the parameter choice, but the relative order of  $\phi_3 \rightarrow \phi_5$  and  $\phi_2 \rightarrow \phi_4$  is sensitive to the parameters employed. This uncertainty coupled with the inability of the Hückel method to distinguish singlet and triplet states suggests the application of a more suitable procedure. It now remains to be determined if the "simplified" s.c.f. procedure is superior for this purpose.

**S.c.f. Calculations.**<sup>11</sup>—Electron repulsion can be included by using a self-consistent field method. The general s.c.f. method, in the LCAO approximation, which has been utilized in purely theoretical calculations of the electronic structure of small molecules, is too cumbersome for application to large molecules. A semiempirical modification has been developed which provides a straightforward computational framework.<sup>12</sup> It is this method which is here designated "the s.c.f. method" and to which all subsequent reference is made.

In the s.c.f. method the orbital energies are determined by diagonalizing the **F** matrix. In contrast to the **H** matrix in the Hückel method, the elements of the **F** matrix depend upon the  $c_{ip}$  coefficients. Consequently, an iterative procedure must be employed. An initial set of molecular orbitals of the form given in eq. 1 is assumed. These are generally obtained by a Hückel calculation, but need not be so determined. The elements of the **F** matrix are

$$F_{pp} = \alpha_p + \frac{1}{2}P_{pp}\gamma_{pp} + \sum_{q \neq p} P_{pq}\gamma_{pq}$$

$$F_{pq} = \beta_{pq} - \frac{1}{2}P_{pq}\gamma_{pq} \quad p \neq q$$

$$P_{pq} = 2 \sum_i c_{ip}c_{iq} \quad (\text{sum over all occupied orbitals})$$

The **F** matrix is then computed and diagonalized. The resultant  $c_{ip}$  are then used to calculate a new **F** matrix. This procedure can be programmed and the iteration repeated until the desired degree of "self-consistency" is obtained.

In place of the two  $\alpha_p$  and  $\beta_{pq}$  parameters that appear in the Hückel theory, in the s.c.f. method four semiempirical parameters are employed. These are the quan-

(11) For a critical review of semiempirical methods and a collection of pertinent reprints, see R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

(12) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953), reprinted in ref. 11.

ties:  $\alpha_p = \int \chi_p H^{\text{core}} \chi_p d\tau$  and  $\beta_{pq} = \int \chi_p H^{\text{core}} \chi_q d\tau$ , in addition to the Coulomb repulsion integrals,  $\gamma_{pq}$ , and the valence state ionization potentials,  $W_p$ . It has been asserted from a detailed study of aniline that the s.c.f. results are "not so sensitive to the parameter choice as are the results of the Hückel method."<sup>13</sup> It must now be determined if this is also true in the case of the acetylacetonate ion in which an additional complication due to the metal ion charge is present.

**Parameter Evaluation.**—The two-center repulsion integrals,  $\gamma_{pq}$ , are dependent upon the geometry. The geometry of the chelate ring in ferric acetylacetonate<sup>14</sup> was chosen for the acetylacetonate ion. The interatomic distances are listed in Table II. A number of prescriptions have been devised for evaluating  $\gamma_{pq}$ ,<sup>11</sup> but the results are not sensitive to the procedure used. In calculation IIa, the formulas of Roothaan<sup>15</sup> were employed, but the effective atomic numbers were adjusted semiempirically from the expression<sup>16</sup>

$$Z_p = \frac{\gamma_{pp}}{5.324}$$

 TABLE II  
 PARAMETER CHOICE FOR S.C.F. CALCULATIONS

	Interatomic distance, Å.	$\gamma_{pq}$ , e.v.		
		IIa	IIb	IIc
$O_1-C_2$	1.280	8.521	8.47	8.47
$O_1-C_3$	2.310	5.644	5.91	5.91
$O_1-C_4$	2.981	4.536	4.82	5.12
$O_1-O_5$	2.840	4.823	4.95	5.98
$C_2-C_3$	1.390	7.723	7.53	7.52
$C_2-C_4$	2.553	5.095	5.33	5.56
$M-O_1$	1.950			
$M-C_2$	2.972			
$M-C_3$	3.235			
	$W_p$ , e.v.	$\gamma_{pp}$ , e.v.		
		IIa	IIb, IIc	
(C)	11.42	10.84	11.08	
(O)	17.21	14.52	14.52	

In IIb, the formulas of Anno, *et al.*,<sup>17</sup> were used for all but  $\gamma_{15}$ . The effect of changing the geometry is largely evidenced in the value of this quantity. In calculation IIc, the Anno formulas were used with a geometry in which the ligand bond angles were set at  $120^\circ$ . A very large value of  $\gamma_{15}$  was also chosen in this calculation.

In the expression

$$\alpha_p = -W_p - \sum_{q \neq p} \gamma_{pq} - \sum_{r \neq p} (r/pp)$$

the index  $q$  refers to atoms in the  $\pi$ -framework while the index  $r$  includes all atoms in the molecule. In calculations IIa,b,c, the penetration integrals ( $r/pp$ ) and the metal ion charge were neglected. The effects of this neglect are considered below.

The nearest neighbor approximation is used for  $\beta_{pq}$ ; for a C-C distance of 1.39 Å.,  $\beta_{C-C} = -2.42$  e.v.<sup>16</sup> The  $\beta_{C-O}$  was computed from Kon's formula<sup>18</sup>

(13) I. Fischer-Hjalms, *Arkiv Fysik*, **21**, 123 (1962), reprinted in ref. 11.

(14) R. B. Roof, *Acta Cryst.*, **9**, 781 (1956).

(15) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(16) R. L. Miller, P. G. Lykos, and H. N. Schmeising, *J. Am. Chem. Soc.*, **84**, 4623 (1962).

(17) T. Anno, I. Matubara, and A. Sodo, *Bull. Chem. Soc. Japan*, **30**, 168 (1957).

(18) H. Kon, *ibid.*, **28**, 275 (1955); reprinted in ref. 11.

as  $-2.00$  e.v. Changing this to  $-2.20$  e.v. increased the transition energies by about  $0.1$  e.v. The values of the parameters used are listed in Table II and the results are summarized in Table III.

TABLE III  
S.C.F. RESULTS

	IIa	IIb	IIc	Exptl.
$S_1 \leftarrow S_0$ , e.v.	4.533	4.362	4.144	4.25
$T \leftarrow S_0$ , e.v.	2.700	2.440	2.302	3 (?)
$f(S_1 \leftarrow S_0)$	0.368	0.416	0.322	0.19
$S_2 \leftarrow S_0$				
$\left\{ \begin{array}{l} \phi_3 \rightarrow \phi_5, \text{ e.v.} \\ \phi_2 \rightarrow \phi_4, \text{ e.v.} \end{array} \right.$	$\left\{ \begin{array}{l} 6.909 \\ 6.626 \end{array} \right.$	$\left\{ \begin{array}{l} 6.743 \\ 6.467 \end{array} \right.$	$\left\{ \begin{array}{l} 6.636 \\ 6.354 \end{array} \right.$	$>6.4$
$P_{11}$	1.663	1.663	1.628	
$P_{22}$	0.641	0.671	0.702	
$P_{33}$	1.391	1.332	1.340	

### Discussion

The lowest  $\pi-\pi^*$  transition,  $S_1 \leftarrow S_0$ , is observed at  $4.25$  e.v. in the spectra of a large group metal acetylacetonates.<sup>2</sup> The energy of the next higher transition,  $S_2 \leftarrow S_0$ , is not always known, but in most cases it exceeds  $6.4$  e.v. In the copper acetylacetonate spectrum, the transition at  $6.2$  e.v. has been assigned as  $S_2 \leftarrow S_0$ .<sup>4</sup> The position of the lowest triplet state is uncertain, but in the phenyl-substituted acetylacetonate ions, benzoylacetonate, and dibenzoylmethide, the  $T \rightarrow S_0$  transitions have been observed at  $2.7$  and  $2.5$  e.v., respectively.<sup>19</sup> The shoulder at  $3.2$  e.v. in the absorption spectrum of sodium acetylacetonate may be due to  $T \leftarrow S_0$ .<sup>6</sup> The lowest triplet state energy is then estimated to be about  $3$  e.v. It can be seen in Table III that, in general, the transition energies and oscillator strengths ( $f$ ) obtained in all three s.c.f. calculations are in reasonable agreement with experiment, and that in particular the  $S_2 \leftarrow S_0$  and  $T \leftarrow S_0$  energies obtained in IIa correspond to experiment as well as can be expected. However, in all three examples the  $S_1-T$  split is  $\sim 2$  e.v. instead of the  $1.25$  e.v. observed.

In order to determine if this large  $S_1-T$  separation results from a poor choice of  $\alpha_p$  (due perhaps to the neglect of penetration integrals and/or metal ion charge), a systematic variation of these parameters was made. The effect of the variation of  $\alpha_p$  on the  $S_1 \leftarrow S_0$  and  $T \leftarrow S_0$  transition energies is indicated in Fig. 2 and 3. If we choose to set the  $S_1 \leftarrow S_0$  exactly at  $4.25$  e.v., then the highest value of  $T \leftarrow S_0$  obtainable is  $2.1$  e.v. If we choose  $4.5$  e.v. for  $S_1 \leftarrow S_0$ , then the best value for  $T \leftarrow S_0$  is  $2.7$  e.v. It can be seen in Table IV that in

TABLE IV  
EFFECT OF  $\alpha_p$  ON TRANSITION ENERGIES  
 $\alpha_1 = 0^a$

$S_1 \leftarrow S_0 = 4.25$ e.v.			$S_1 \leftarrow S_0 = 4.50$ e.v.		
$\alpha_3$	$\alpha_2$	$T \leftarrow S_0$	$\alpha_3$	$\alpha_2$	$T \leftarrow S_0$
-5.0	-2.5	1.70	-5.0	-1.7	2.15
-3.0	-1.0	1.70	-3.0	-0.2	2.30
-1.0	0.5	1.90	-1.0	1.2	2.50
0	1.2	2.00	0	1.8	2.55
2.0	2.4	2.10	2.0	3.0	2.65
4.0	3.6	2.05	4.0	4.2	2.60
5.0	4.1	1.95	5.0	4.8	2.60
7.0	5.2	1.80	7.0	5.8	2.25

<sup>a</sup> All other parameters as in calculation IIa; values in e.v.

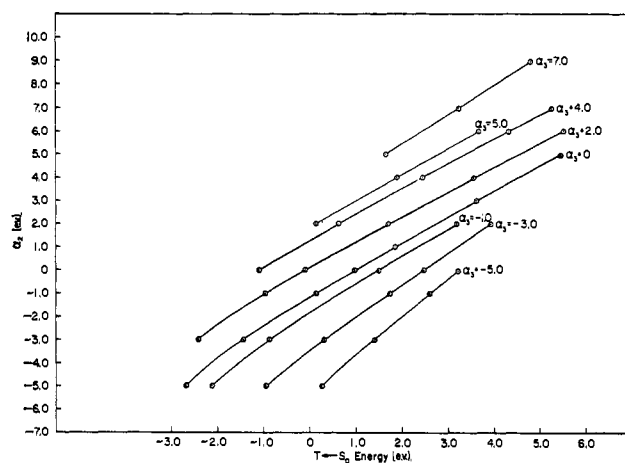


Fig. 2.—Variation in  $S_1 \leftarrow S_0$  energy with  $\alpha_p$  ( $\alpha_1 = 0$ ).

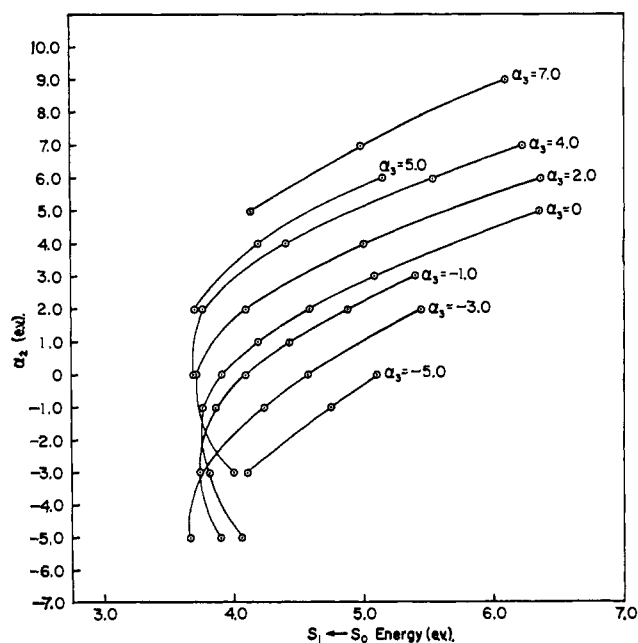


Fig. 3.—Variation in  $T \leftarrow S_0$  energy with  $\alpha_p$  ( $\alpha_1 = 0$ ).

either event, a number of combinations of  $\alpha_p$  will yield nearly the same results. It is noteworthy that although in some cases, for a given  $\alpha_1$  and  $\alpha_3$ , two values of  $\alpha_2$  correspond to the same  $S_1 \leftarrow S_0$  energy, only one of these will give a reasonable value of  $T \leftarrow S_0$ . The computed  $S_1-T$  splitting can be reduced, but only by sacrificing agreement with the observed  $S_1 \leftarrow S_0$  and  $T \leftarrow S_0$  energies.

The inclusion of configuration interaction does not alter the results significantly. Even though the  $\phi_2 \rightarrow \phi_4$  and  $\phi_3 \rightarrow \phi_5$  singlet states are nearly degenerate, the matrix element connecting the two states is very small (ca.  $0.1$  e.v.).

**Neglect of Penetration Integrals and Metal Ion Charge.**—From the foregoing it is seen that calculation IIa, in which  $\alpha_2 - \alpha_1 = 3.43$  e.v. and  $\alpha_3 - \alpha_1 = 2.58$  e.v., very nearly represents the optimum obtainable with this s.c.f. formalism. These  $\alpha_p$  were computed with all penetration integrals neglected and by assuming the metal ion was without influence. It has been found that the protonation of pyridine could best be described by a point charge model, *i.e.*, by reducing each  $\alpha_p$  by the electrostatic potential due to a bare

(19) R. E. Whan and G. A. Crosby, *J. Mol. Spectry.*, **8**, 315 (1962).

proton.<sup>20</sup> In view of the observed insensitivity of the acetylacetonate  $\pi$ - $\pi^*$  transition energies to the metal ion charge<sup>2</sup> it may be assumed that the oxygen lone pairs shield the positive charge to some extent. The effective charge to be used in the sodium acetylacetonate case is probably somewhat less than +1 and this quantity is not changed much in the divalent and trivalent metal chelates involving acetylacetonate. A similar conclusion has been reached for the effect of metal ion charge on pyridine ligands.<sup>21</sup> The reductions of  $\alpha_p$  for atoms 1, 2, and 3, due to a +1 charge are 6.73, 4.84, and 4.45 e.v., respectively.

Although accurate values of the penetration integrals have not been evaluated, the effect of including such integrals can be estimated. The oxygen atoms are bonded to one other atom, while each carbon in the  $\pi$ -framework is bonded to three other atoms. If each penetration integral is equal to about 1 e.v., then the 2 e.v. lowering at C-2 and C-3 by the penetration integrals is partially offset by the electrostatic effect at O<sub>1</sub>, *i.e.*, the two effects tend to cancel. It is then not surprising that the results obtained by neglecting these two opposing effects are fairly good.

**Charge Distribution.**—Both the Huckel and s.c.f. methods predict a markedly inhomogeneous  $\pi$ -electron density on the carbon atoms. In accord with the high reactivity of the 3-positions toward electrophilic reagents, the charge density is higher on C-3.<sup>22</sup> The deactivation of the ring when the methyl groups are replaced by trifluoro groups might then be explained by the lowering of  $\alpha_2$ . A reduction of  $\alpha_2$  by 2 e.v. would reduce the charge on C<sub>3</sub> to near unity, but the  $S_1 \leftarrow S_0$  transition energy would be decreased by 1 e.v. Such a shift is not observed either in the free enols or the metal complexes containing trifluoro- or hexafluoroacetylacetonate ligands.

In the variable electronegativity modification of the s.c.f. method (v.e.s.c.f.), the  $\alpha_p$  and  $\gamma_{pq}$  are functions of the charge densities  $P_{pp}$ .<sup>23</sup> Utilization of this procedure generally leads to a diminution of the charge inhomogeneities without affecting the transition energies appreciably. It is, however, unlikely that the application of the v.e.s.c.f. method to the acetylacetonate ion will lead to improved results. The effect of  $\alpha_p$  variation has already been considered (Fig. 2 and 3). Although a more uniform charge distribution can be obtained by adjusting  $\alpha_p$ , the resultant  $T \leftarrow S_0$  transition energy will be very small (or negative!). The changes in the off-diagonal  $\gamma_{pq}$  are negligible and the diagonal

(20) S. Mataga and N. Mataga, *Bull. Chem. Soc. Japan*, **32**, 511 (1959).

(21) S. Mataga and N. Mataga, *Z. physik. Chem. (Frankfurt)*, **33**, 374 (1962).

(22) J. P. Collman, *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington 25, D. C., 1963, p. 28.

(23) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

$\gamma_{pp}$  are included in  $\alpha_p$ . Therefore, in cases of very heteropolar  $\pi$ -systems the s.c.f. procedure may suffer from the same defect as the Hückel method, *viz.*, the failure to obtain good results for both transition energies and ground-state properties.

**Open-Shell S.c.f. Calculations for  $T \leftarrow S_0$ .**—In the calculations described above, the excitation energies were computed by promoting an electron from a doubly occupied orbital to an empty (virtual) orbital. For singlet-singlet transitions this is the only procedure within the s.c.f. formalism. In the case of  $T \leftarrow S_0$ , an alternative exists—the open-shell procedure in which the energies of the ground state ( $S_0$ ) and excited state (T) are separately computed.<sup>24</sup> The  $T \leftarrow S_0$  energy corresponding to calculation IIa determined in this way is 2.34 e.v. The agreement with experiment is poorer and the usual (closed-shell) technique appears to be preferable.

### Conclusions

The results indicate that the simplified version of the s.c.f. method is adequate for the determination of the transition energies and intensities, but that the calculated charge distribution may not be quantitatively reliable. The prescriptions commonly used for the determination of the s.c.f. parameters are suitable, largely due to the relative insensitivity of the s.c.f. results to the parameter choice. The s.c.f. and Hückel methods are in agreement in the assignment of  $S_1 \leftarrow S_0$  as  $\phi_3 \rightarrow \phi_4$ , but differ in the  $S_2 \leftarrow S_0$  assignment. This transition is assigned as  $\phi_3 \rightarrow \phi_5$  or  $\phi_2 \rightarrow \phi_4$  by the Hückel method depending on the parameters used, while the s.c.f. results point to  $\phi_2 \rightarrow \phi_4$  being slightly lower in energy than  $\phi_3 \rightarrow \phi_5$ . This conclusion is of importance in the calculations of the electronic structure of metal complexes with two and three acetylacetonate ligands. In this connection it must be kept in mind that while the transition energies are not very dependent on the parameter choice, the s.c.f. orbital energies do vary greatly with  $\alpha_p$ . Consequently, if ligand orbitals are to be combined with metal orbitals in LCAO-MO calculations, considerable uncertainty in ligand orbital energies must be expected.

A description of the s.c.f. program used in this work and a FORTRAN listing of the program are available from the author.

**Acknowledgments.**—The matrix diagonalization routine was obtained through the kindness of Dr. H. E. Simons of the Central Research Department, Experiment Station, E. I. du Pont de Nemours Co. This work would not have been possible without the programming assistance of Professor Robert Baker of the University of Arizona Numerical Analysis Laboratory.

(24) O. W. Adams and P. G. Lykos, *J. Chem. Phys.*, **34**, 1444 (1961).