

ing the direct interactions of the reaction group, ring carbons and methyl groups together.

Conclusions

The semi-empirical self-consistent LCAO-MO method employed in this investigation seems capable of explaining the relative basicities of the methyl benzenes in strong acid solutions mainly on the basis of hyperconjugative stabilization of the cations by the substituent methyl groups. Equally consistent results would not be obtained from naïve molecular orbital treatments. The most important theoretical factor introduced by the improved methods is unquestionably charge redistribution, particularly in the ions.

The quantitative results obtained agree well with empirical expectations for electrophilic aromatic reactions and with predictions from simple valence bond theory. Agreement with the former extends from the qualitative notions of the effects of electron donors as functions of position of substitution, to the quantitative separations afforded by linear free energy equations, *e.g.*, *ρσ meta* to *para* resonance ratios, and C-C bond, relative to C-H bond, hyperconjugation. The intermediate theoretical results, as well as the total equilibrium constants

calculated therefrom, are found to be consistent with experiment wherever comparisons are available. The importance of C-C bond hyperconjugation is strongly indicated in this study, under acceptance of the model. Compared to the C-H bond effect, it appears to be about three-fourths as effective in *para* position hyperconjugation (and about the same in the *ortho* position) for a reaction series which may be derived from the theoretical data.

Extension of this model to test further the importance of hyperconjugation in molecules where it might be expected to contribute appreciably as a stabilizing effect would be desirable. Other methyl-substituted aromatics such as the naphthalenes and azulenes, for the ions of which isovalent hyperconjugation structures may be written, are of particular interest. Studies of these systems and an attempt to refine the inductive model for comparisons of the results by both methods are contemplated for the near future.

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[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS]

Electronic States in the C₄ Molecule^{1a}

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An s.c.f.-l.c.a.o.-m.o. ground state wave function for the lowest ³Σ_g⁻ and for an excited ¹Σ_g⁺ state of C₄ is reported. All twenty-four electrons are considered in this computation. The internuclear distance assumed for all the states is 1.28 Å. for the three bonds of C₄, following some earlier prediction. Diagrams are presented which give a pictorial representation of the molecular orbitals obtained. An l.c.a.o.-m.o. computation was done for the ¹Δ_g and ¹Σ_g⁺ states and for a second ¹Σ_g⁺ excited state. A discussion is given on the expected bond variation for the different excited states, as compared with the ground state. Estimates are made of the centers of gravity for the two lowest ³Π and ¹Π states. It is concluded that the ³Σ_g⁻ should be the ground state as earlier suggested by Pitzer and the author.

Introduction

Some time ago Pitzer and the author² presented evidence that the C₄ molecule is linear and that its ground state should have ³Σ_g⁻ symmetry. This conclusion was based on a refinement^{2b} of the Hückel π-electron model.³ The correct assignment is of importance, since all the C_n molecules with *n* even and > 2 were predicted as having the same species of ground state.

In the present paper we present a complete s.c.f.-l.c.a.o.-m.o. computation for the C₄ molecule. All the integrals for the 24 electrons were accurately computed using McLean's Linear Molecules Program. The basis set for the wave function consists for each atom of one 1s, one 2s, one 2p_σ and one 2p_π Slater-type orbital (s.t.o.), with the same orbital exponents as were found best for the ground state of the C₂ molecule.⁴ We examined several electronic

configurations and thus we can present a theoretical computation for a discussion of the symmetry and the electronic configuration of the ground state for the C₄ molecule.

The internuclear distances were chosen as 1.28 Å., and these may be somewhat in error, since there should be bond alternation in various degrees in the different states. The value of 1.28 Å. was taken from the C₃ molecule⁵ and is the same as that postulated for C₄ in the original work.¹

Analysis of the Resulting Wave Functions.—

The ground state electron configuration is supposed to be

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^2 \quad (a)$$

where clearly the electron pairs in the first four m.o.'s are expected to correspond essentially to atomic 1s² closed shells of the C atoms. The electrons in the remaining three σ_g and two σ_u m.o.'s provide for the σ bonds and two essentially non-

(1) (a) This work was supported by the National Science Foundation. (b) I. B. M. Research Laboratory, San Jose, California.

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TABLE I
 COEFFICIENTS FOR THE ${}^3\Sigma_g^-$ (a) WAVE FUNCTION^a

Symmetry orbitals	$\epsilon(1\sigma_g) =$ -11.29700	$\epsilon(2\sigma_g) =$ -11.22332	$\epsilon(3\sigma_g) =$ -1.03428	$\epsilon(4\sigma_g) =$ -0.81538	$\epsilon(5\sigma_g) =$ -0.39567	$\epsilon(1\pi_u) =$ -0.36352
$1s_1 - 1s_4$	-0.00740	0.70491	0.05781	-0.10968	-0.11226
$2s_1 + 2s_4$.00251	.01100	-.14875	.36093	.60297
$2p\sigma_1 - 2p\sigma_4$.00083	.00429	-.10208	.15206	-.48956
$1s_2 + 1s_3$	-.70447	-.00749	.16724	.02414	.03419
$2s_2 + 2s_3$	-.00982	-.00390	-.48529	-.09028	-.19931
$2p\sigma_2 - 2p\sigma_3$.00063	.00208	-.09943	-.42038	.22841
$2p\pi_1 + 2p\pi_4$	-0.22571
$2p\pi_2 + 2p\pi_3$	-0.53231
Symmetry orbitals	$\epsilon(1\sigma_u) =$ -11.29506	$\epsilon(2\sigma_u) =$ -11.23332	$\epsilon(3\sigma_u) =$ -0.90156	$\epsilon(4\sigma_u) =$ -0.40420	$\epsilon(5\sigma_u) =$ 0.53978	$\epsilon(1\pi_g) =$ -0.17582
$1s_1 - 1s_4$	-0.00633	0.70491	-0.11604	0.11980	0.05576
$2s_1 - 2s_4$.00403	.01115	.33900	-.63868	-.45130
$2p\sigma_1 + 2p\sigma_4$.00180	.00436	.17784	.36458	-.53669
$1s_2 - 1s_3$	-.70448	-.00617	-.11024	-.06181	-.15081
$2s_2 - 2s_3$	-.01774	-.00548	.35467	.35041	1.32394
$2p\sigma_2 + 2p\sigma_3$	-.00148	.00137	-.21669	-.12983	.30041
$2p\pi_1 - 2p\pi_4$	0.48885
$2p\pi_2 - 2p\pi_3$	0.44837

^a ϵ 's are given in a.u. Each coefficient applies to each a.o. of the symmetry orbital.

 TABLE II
 COEFFICIENTS FOR THE ${}^1\Sigma_g^+$ (e) WAVE FUNCTION^a

Symmetry orbital	$\epsilon(1\sigma_g) =$ -11.13671	$\epsilon(2\sigma_g) =$ -11.05212	$\epsilon(3\sigma_g) =$ -0.98953	$\epsilon(4\sigma_g) =$ -0.72970	$\epsilon(5\sigma_g) =$ -0.42450	$\epsilon(1\pi_u) =$ -0.33754
$1s_1 + 1s_4$	0.70455	0.00891	0.09701	-0.10188	0.09466
$2s_1 + 2s_4$.01124	.00331	-.29164	.40708	-.50939
$2p\sigma_1 - 2p\sigma_4$.00336	.00112	-.14842	.10551	.45328
$1s_2 + 1s_3$.00875	-.70434	.14720	.08819	-.02412
$2s_2 + 2s_3$	-.00353	-.01084	-.40751	-.32528	.13065
$2p\sigma_2 - 2p\sigma_3$.00169	.00220	.03482	-.34984	-.24010
$2p\pi_1 + 2p\pi_4$	-0.27259
$2p\pi_2 + 2p\pi_3$	-0.50630
Symmetry orbital	$\epsilon(1\sigma_u) =$ -11.13673	$\epsilon(2\sigma_u) =$ -11.05051	$\epsilon(3\sigma_u) =$ -0.92755	$\epsilon(4\sigma_u) =$ -0.44533	$\epsilon(5\sigma_u) =$ 0.28946	$\epsilon(1\pi_g) =$ 0.01510
$1s_1 - 1s_4$	0.70455	-0.00754	-0.12587	-0.11257	0.05544
$2s_1 - 2s_4$.01245	-.00477	.39757	.60051	-.46117
$2p\sigma_1 + 2p\sigma_4$.00346	-.00209	.18097	-.39421	-.54355
$1s_2 - 1s_3$.00762	.70437	-.10495	.06760	-.15267
$2s_2 - 2s_3$	-.00545	.01755	.31346	-.36260	1.32987
$2p\sigma_2 + 2p\sigma_3$.00077	-.00120	-.18244	.11455	0.26933
$2p\pi_1 - 2p\pi_4$	0.55161
$2p\pi_2 - 2p\pi_3$	0.35494

^a ϵ 's are given in a.u.

bonding pairs. Finally we have the six π electrons distributed four in the $1\pi_u$ and two in the $1\pi_g$ molecular orbitals. This configuration gives rise to a ${}^3\Sigma_g^-$, ${}^1\Delta_g$, and ${}^1\Sigma_g^+$ state, here given in order of increasing energy. We have also considered other configurations near the ground state. These are (omitting the first six m.o.'s)

$$(b) \dots 4\sigma_g^2 4\sigma_u^2 5\sigma_g^1 1\pi_u^4 1\pi_g^3; {}^1{}^3\Pi_g \quad (b)$$

$$(c) \dots 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^3; {}^1{}^3\Pi_u \quad (c)$$

$$(d) \dots 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^4; {}^1\Sigma_g^+ \quad (d)$$

$$(e) \dots 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 5\sigma_u^2; {}^1\Sigma_g^+ \quad (e)$$

The configurations are called (a), (b), (c), (d) and (e) and the labelling corresponds to the order of increasing energy.

We computed the s.c.f.-l.c.a.o.-m.o. wave function for the ${}^3\Sigma_g^-$ state of configuration (a). Then using the s.t.o.'s coefficients of that state we computed the l.c.a.o.-m.o. energies for the ${}^1\Delta_g$ (a), ${}^1\Sigma_g^+$ (a), ${}^1\Sigma_g^+$ (d) and ${}^1\Sigma_g^+$ (e) states. Finally in

order to gain an idea of the reorganization effect (= energy difference between the l.c.a.o.-m.o. computation and the s.c.f.-l.c.a.o.-m.o. computation for the same state) we have computed the s.c.f.-l.c.a.o.-m.o. wave function for the ${}^1\Sigma_g^+$ state of configuration e.

The coefficients and the orbital energies for the ${}^3\Sigma_g^-$ (a) and ${}^1\Sigma_g^+$ (e) states are given in Tables I and II. The z axis is always pointing in the same direction for all four atomic centers.

Let us comment briefly on the two s.c.f. wave functions. The ${}^3\Sigma_g^-$ state has the four lowest m.o.'s with approximately the same orbital energies ϵ (as expected), but the ϵ 's corresponding to ls of the inner carbon atoms are lower than those of the exterior carbon atom by about 2 e.v. The same energy difference holds also for the ϵ 's of the ${}^1\Sigma_g^+$ (e) state. The reason is doubtless that the field inside the molecule is not the same as on the two ends (end-effect), and this is true even for the closed

shells. We note also that for the energies of the inner shells the u, g classification loses its importance, but instead the geometrical location of the atom in the molecule is the important factor; that is to say, $\epsilon(1\sigma_g) = \epsilon(1\sigma_u)$, $\epsilon(2\sigma_g) = \epsilon(2\sigma_u)$.

The next set of m.o.'s are the $3\sigma_g$, $3\sigma_u$ and $4\sigma_g$ all having comparable energies, and thus we group them together in this discussion. The $3\sigma_g$ m.o. provides strong σ bonding between the two central atoms and also considerable bonding of these to the outer atoms. At each region of overlap, the sign of the sp hybridization is such as to favor strong bonding. The $3\sigma_u$ m.o. provides strong σ bonding between the first two and the last two carbon atoms of C₄ and is weakly antibonding between the second and the third carbon atom where it has one nodal plane. The signs of the sp hybridizations are such as to strengthen the bonding and weaken the antibonding. The last of the orbitals of this group, the $4\sigma_g$, is bonding between the first and second, second and third and third and fourth carbon atom. The sp hybridization is roughly comparable for the $3\sigma_g$ and $4\sigma_g$ molecular orbitals but more pronounced in the $3\sigma_u$.

Finally the last four m.o.'s, which can be grouped together because of their energy similarity, include the $4\sigma_u$, $5\sigma_g$, $1\pi_u$ and $1\pi_g$ m.o.'s. The $4\sigma_u$ is weakly antibonding but may be described as nearly non-bonding; $5\sigma_g$ is essentially non-bonding, with a very weak central bond. The $1\pi_u$ is mostly concentrated at the center of the molecule and extends over the whole molecule as expected. The $1\pi_g$ is strongly antibonding at the center of the molecule but strongly bonding for each outer pair of atoms. From this we might say that the C₄ molecule in the $^3\Sigma_g^-$ corresponds to the structure :C=C=C=C: as previously reported.²

These observations can be surveyed by looking at Fig. 1 where all these results are given in a highly simplified way.⁶

The reorganization effect for the $^1\Sigma_g^+$ (e) has lowered its total energy by about 1.7 e.v. for the internuclear distances of 1.28 Å. We note that the $4\sigma_g$ m.o. in the $^1\Sigma_g^+$ (e) state has shifted part of its electron cloud from the middle to the sides of the molecule, thus weakening the middle bond. The $5\sigma_g$ m.o. shows no major redistribution of charges. The $4\sigma_u$ in the $^1\Sigma_g^+$ (e) shifts its charge from the sides of the molecule to the middle, if compared with the $4\sigma_u$ in the $^3\Sigma_g^-$ (a) state. The $5\sigma_u$ is essentially as it was in the unoccupied $5\sigma_u$ m.o. for the $^3\Sigma_g^-$ (a) state. The $1\pi_u$ m.o. in the $^1\Sigma_g^+$ (e) state has lower density in the middle of the molecule than the $1\pi_u$ of the $^3\Sigma_g^-$ (e) state. The difference in the coefficients is not great, but we must remember that there are four electrons in the $1\pi_u$ (in view of the π_u^+ and π_u^- degeneracy).

(6) The 2s a.o.'s are represented by a circle, the 2p a.o.'s by two circles. The radius of the schematized atomic orbital is chosen such as to give an overlap area proportional to the overlap integrals, when two equal atomic orbitals are centered on the nearest neighboring atoms. With our orbital exponents, the overlap integrals at 1.28 Å are: $S(2s,2s) = 0.46$, $S(2p\sigma,2p\sigma) = 0.32$, $S(2p\pi,2p\pi) = 0.30$. When these standard radii for the atomic orbitals were obtained, we multiplied them by the corresponding coefficients given in Table I and II and plotted them then as in Fig. 1. We omitted the lowest four m.o.'s, since the corresponding diagrams can be obtained at sight by inspection of the coefficients.

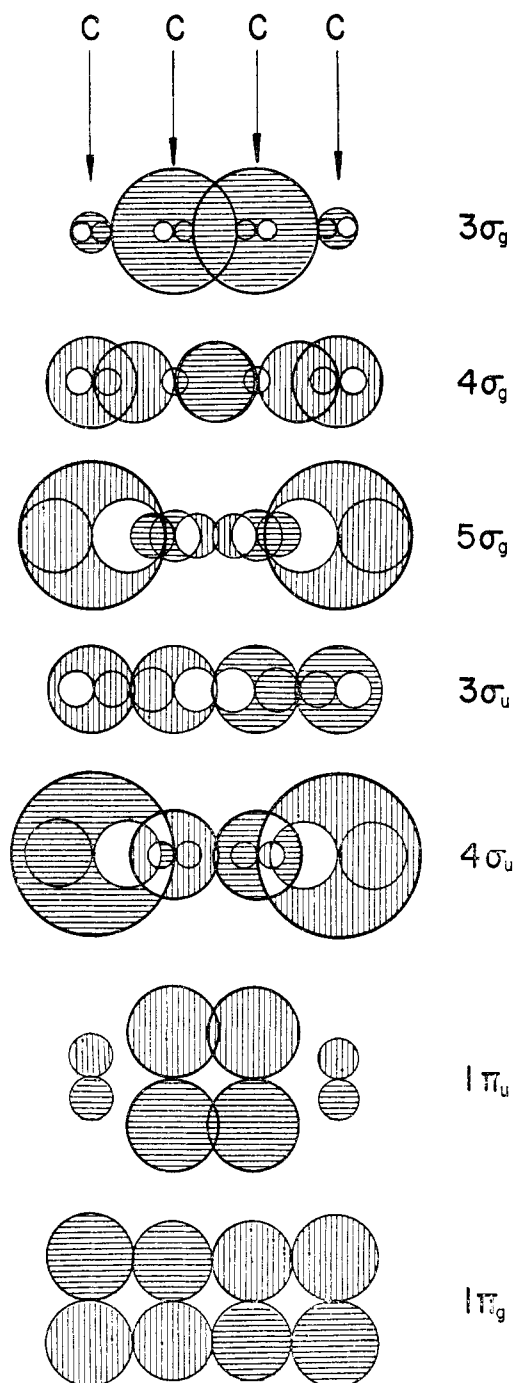


Fig. 1.—Diagrammatic representation of the molecular orbitals for the $^3\Sigma_g^-$ state. The different directions of the shading represent positive and negative signs in the atomic orbitals. When both positive and negative areas are superimposed, blanks are given. When two or more atomic orbitals contribute to the same area with same sign, no particular indication is given in the diagram. The contribution of the 1s atomic orbitals is not given since it is small.

Let us start with some comment on the resulting total energies obtained in the l.c.a.o.-m.o. and/or the s.c.f.-l.c.a.o.-m.o. approximation. The energies are collected in the third column of Table III.

The two computations for the $^1\Sigma_g^+$ (e) state give the energy stabilization due to the reorganization

TABLE III

COMPUTED AND ESTIMATED ENERGIES FOR GROUND STATE AND EXCITED STATES IN C_4 WITH 1.28 Å BOND LENGTH

State	Computation Method	Total energy (a.u.)	Estimated excitation energy (e.v.) from the ${}^3\Sigma_g^-$
${}^1\Sigma_g^+$ (e)	L.c.a.o.-m.o.	-149.56516	33.0
${}^1\Sigma_g^+$ (e)	S.c.f.-l.c.a.o.-m.o.	-149.62863	
${}^1\Sigma_g^+$ (d)	L.c.a.o.-m.o.	-150.44457	9.0
${}^1\Pi_u$ (c)	5.2
${}^3\Pi_u$ (c)	4.2
${}^1\Pi_u$ (b)	4.5
${}^3\Pi_u$ (b)	3.5
${}^1\Sigma_g^+$ (a)	L.c.a.o.-m.o.	-150.79648	1.0
${}^1\Delta_g$ (a)	L.c.a.o.-m.o.	-150.81944	0.5
${}^3\Sigma_g^-$ (a)	S.c.f.-l.c.a.o.-m.o.	-150.84363	0.0

effect in the excited states as compared to the ground state. For this state, the two electrons were promoted from a $1\pi_g$ orbital to a $5\sigma_g$ molecular orbital. As a result, the middle bond is expected to be longer than 1.28 Å. The same type of bond variation should be expected in the ${}^1\Sigma_g^+$ (d). For the ${}^1,{}^3\Pi$ states of configuration b and c again we would expect a lengthening of the central bond for the same reason as above. The two configurations b and c should have not too different bond lengths, and small energy separation (which might possibly be increased by mutual configuration interaction). We estimate the total energy for the center of gravity of the two ${}^1,{}^3\Pi_g$ states of the b configuration to be around -150.70 a.u. and the center of gravity for the two ${}^1,{}^3\Pi_u$ states of the c configuration at about -150.66 a.u. Possibly, the splitting between single and triplet states is of the order of 1 e.v., but we think that we cannot make any reliable estimates at present, since the bond variation should definitely be taken into account. This is somewhat difficult since we do not have any experimental value on the C_4 molecule.

Conclusions

The energy difference from the ${}^3\Sigma_g^-$ ground state of C_4 to the excited states is given in the last column of Table III. These estimates and calculations are given for the internuclear distances of 1.28 Å. This should be kept in mind throughout the reading of this work. Considerable variations in bond length are expected for the excited state which approximates the structure $C\equiv C-C\equiv C$, and this should introduce non-negligible variation in the energy. The linearity of C_4 is assumed throughout this work. Whereas we are confident that this is true for the ground state and other configurations, this might not be true for the ${}^1\Sigma_g^+$ (d) configuration.

Let us comment on the reorganization effect. We define the reorganization effect of an electronic state B relative to a standard electronic state A (generally the ground state) the deformation in the molecular orbitals of the state B (relative to the state A) necessary to minimize the energy of the state B to the same extent as for the state A. In other words, if we perform an s.c.f. computation for the state A and then we use the same molecular orbitals of the state A to compute the energy of the state B, we do not allow the state B to be deformed

in its molecular orbitals in such a way as to have the best average field. The states A and B are not equally treated. This restriction is released by performing an s.c.f. computation for the state B. This is the first contribution to the reorganization effect. A second contribution is given by altering the basis set of the state B by optimization of the orbital exponents of the s.t.o.'s and by inclusion or exclusion of one or more s.t.o.'s. Finally one should mention that a more general definition of reorganization effect cannot disregard the differences in correlation energy of states A and B.

Clearly there is some degree of artificiality in the definition of the reorganization effect, but it provides a useful and quantitative base for discussion of the variation in hybridization, polarization, etc., when we excite a molecule from the ground state to an excited state. There are no rules, at present, to help in the prediction of the reorganization energy. But one might expect that the reorganization effect is progressively larger between states which have different configurations due to an electron (or electrons) promotion from bonding to less bonding or medium antibonding or strongly antibonding molecular orbitals, and comparatively smaller reorganization is expected between states of the same configuration. The concept of reorganization can be usefully applied to a molecule and its corresponding ions. Here again we expect a large reorganization effect. This is partially confirmed by our finding on the HF ground state and the HF⁺ ground state⁷ where the effect of reorganization is of the order of 2 electron volts.

In this work on C_4 the reorganization effect for the ${}^1\Sigma_g^+$ (e) state is large (about 1.7 electron volts) since we excite two electrons from an antibonding $1\pi_g$ m.o. to a more strongly antibonding $5\sigma_u$ m.o. (Possibly, the computed reorganization effect could have been more extreme if we would have used a larger basis set of s.t.o.'s both in the ${}^3\Sigma_g^-(\alpha)$ and ${}^1\Sigma_g^+$ (e) states.)

If we are correct in our expectation of the magnitude of the reorganization energy, we tentatively predict a small lowering in the ${}^1\Sigma_g^+$ (a) and ${}^1\Delta_g$ (a) state due to reorganization. (Thus in Table III we lower the computed splitting of the ${}^1\Sigma_g^+$ (a) and the ${}^1\Delta_g$ (a) states to the ${}^1\Sigma_g^-(a)$ from 0.63 to 0.5 e.v. and from 1.26 to 1.0 e.v. respectively.) For the other states given in Table III the estimated location is regarded as provisional.

In addition, the absence of correlation energy in our one-electron model computation makes the predictions of the ordering of the excited states even more provisional. As is well known, inclusion of configuration interaction would account for the lack of correlation but would in addition require a computational effort of quite a different order of magnitude.

At any rate we feel that the assignment of the ground state as given previously by Pitzer and the author is substantially correct and the same can be said, but with less confidence, of the relative order of the excited states as given in Table III. This could provide a starting point for experimental work on the spectra of the C_4 molecule.

(7) R. Clementi, to be published in *J. Chem. Phys.*

Finally we note that the gross charge Q obtained as prescribed by Mulliken⁸ gave the charges, $+0.19$, -0.19 , -0.19 , $+0.19$ for the first, second, third and fourth carbon atoms in C_4 .⁹ This might be compared with the charges $+0.20$, -0.40 ,

- (8) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338 (1955).
 (9) E. Clementi and H. Clementi, to be published.

$+0.20$ on the first, second and third carbon atoms in C_3 .⁸

Acknowledgments.—The author is indebted to his wife for her help with the computations of the gross charge and in the drawing of Fig. 1 and to Professor R. S. Mulliken for commenting on this paper.

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Electron Spin Resonance in Molecular Complexes. I. Electronic Splitting and Hyperfine Interactions in the Solid State

BY MONISHA BOSE¹ AND MORTIMER M. LABES

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The resolution of the e.s.r. absorption of several amine-quinone complexes in the solid state establishes the existence of uncoupled spins as a rather general feature of these materials. Hyperfine structure has also been observed. A delineation and discussion of the respects in which the amine-quinones differ from the paramagnetic hydrocarbon-halogen complexes is given. The relationship of e.s.r. data to information regarding electronic conduction in the same materials is also discussed.

I. Introduction

Electron spin resonance (e.s.r.) has been observed in amine-quinone² and hydrocarbon-halogen^{3,4} molecular complexes. Kainer, *et al.*,² explain the observed paramagnetism in terms of an ionic ground state for this strong donor-acceptor (D-A) interaction. The free ions, D^+ and A^- , would each have an unpaired electron, each be in a doublet state and give two independent spins unless they interact strongly in the complexes to give splitting into a diamagnetic singlet and a paramagnetic triplet state.

Bijl, *et al.*,^{2b} in a study of several amine-quinone complexes found a single absorption line in all but one case, the *p*-phenylenediamine-bromanil complex, which had two unresolved lines with g values of 2.0095 and 2.005 at 90°K. Matsunaga⁵ reports clear resolution for *p*-phenylenediamine-chloranil and correlation of the resonance lines with those independently observed for the component ions; he also notes that absorption for N,N,N',N' -tetramethyl-*p*-phenylenediamine-chloranil is highly asymmetric.

We have found similar results for *p*-phenylenediamine-chloranil^{6c}; in this paper the successful resolution of the resonance absorption of several molecular complexes, and several cases of hyperfine structure in these solids are reported.

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(6) (a) M. M. Labes, R. Sehr and M. Bose, *J. Chem. Phys.*, **32**, 1570 (1960); (b) M. M. Labes, R. Sehr and M. Bose, *ibid.*, **33**, 868 (1960); (c) R. Sehr, M. M. Labes, M. Bose, H. Ur and F. Wilhelm, "Proc. Conference on Electronic Conductivity in Organic Solids," Durham, N. C., April 20-22, 1960, Interscience Publishers, Inc., New York, N. Y., to be published (1961); (d) M. M. Labes, R. Sehr and M. Bose, "Proc. International Conference on Semi-conductor Physics," Prague, Czechoslovakia, August 29-September 2, 1960, 850 (1961).

The hydrocarbon-halogen complexes also exhibit paramagnetism but Matsunaga's,³ Singer and Kommandeur's⁴ and our own work^{6c} have uncovered no cases of structure in the resonance spectra. This and other differences in the two types of complexes will be discussed in detail.

II. Experimental

Materials.—The preparation of the complexes and starting materials from which they are derived has been described in previous papers,⁶ with the exception of diaminodurene and N,N,N',N' -tetramethyl-*p*-phenylenediamine. The former was prepared in a manner analogous to that described by Smith,⁷ m.p. 147-148° after two recrystallizations from alcohol. The latter amine after liberation from the dihydrochloride obtained from British Drug House was sublimed three times *in vacuo*, m.p. 46-48°.

Spin Resonance Measurements.—Initial spin resonance experiments were carried out with the standard Varian V4500 EPR spectrometer operating in the X band. The Varian V4560 100 kc. field modulation unit was used in the later stages in conjunction with the Varian V-4531 multi-purpose cavity which enabled the sample temperature to be varied from room down to liquid nitrogen temperatures. The increase in sensitivity and resolution obtained at this higher modulation frequency is obvious in Fig. 1. The spectra were recorded using a very low modulation field and a slow scanning rate. The g values were estimated by comparison with either α,α -diphenyl- β -picrylhydrazyl (D-PPH) or with ultramarine. The line widths reported are between points of maximum slope.

Preliminary studies on some samples indicated that the resonance absorption was not affected by atmospheric oxygen. However, as a precautionary measure, all the samples were studied *in vacuo*. It was necessary however, to use fresh samples as the absorption was found to be modified considerably on storage in some cases. All measurements were performed on microcrystalline material.

III. Results

Figure 1 shows the e.s.r. spectra of *p*-phenylenediamine-chloranil at room temperature. Figure 1a, obtained with a modulation frequency of 400 c./sec. and an amplitude of modulation field of approximately 0.2 gauss, exhibits two absorption peaks with g values of 2.0026 and 2.0056, respectively, corresponding to the uncoupled spins of the donor and acceptor ions (*cf.* Matsunaga).⁵ Figure

(7) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 254.