tric constant close to those of methanol, we observe a slight red shift of the bands of I and IVa–IVd. If the "250 mμ" band arises from the electron-transfer transition (1),[7] the observed red shift in the polar solvent is in accord with the predictions by Bayliss and McRae.[31] The enhancement of the dipole moment accompanying excitation leads to a greater solvent-stabilization of the excited state than the ground state and hence to a shift of the "250 mμ" band to longer wave lengths.

Although the $A_{\text{max.}}$'s are slightly diminished by transfer from the hydrocarbon to the polar solvent, the oscillator strengths are unchanged. The first implication is that the spectra have become more diffuse, again in agreement with Bayliss and McRae.[31] Further, it suggests that there are no specific interactions between solute and solvent which would decrease the resonance stabilization of the ground state and hence the oscillator strength of the electron-transfer band.

In methanol, the bands of I and IVc are shifted slightly to the red, though the shift is not as pronounced as in acetonitrile. The bands of IVb and IVd are shifted slightly to the blue, and the bands of IVa are shifted substantially to the blue. With the exception of the bands of IVc, the oscillator strengths also are diminished.

The experiments in acetonitrile presumably measure the spectral effects to be attributed to generalized polar solvation of these amines. The fact that all the bands in methanol are shifted to the blue relative to their positions in acetonitrile may be interpreted on the basis of hydrogen bonding to the lone pair on nitrogen. Pimentel[32] has discussed the effects of hydrogen bonding on electronic spectra and has predicted a blue shift of bands of I in "acidic" solvents. In this connection it may be noted that Bayliss and McRae[31] have evidently misinterpreted the spectral results of Ungnade,[33] who found a progressive blue shift of the bands of dimethylaniline in the solvent-order cyclohexane, ethanol, water.

If, as Bayliss and McRae[31] assert, refractive index dependent polarization shifts are the only ones to be expected for I, the peaks should shift to the blue in the solvent-order isoöctane, acetonitrile, methanol. In addition, the maxima in methanol (251 mμ) and water (244 mμ[33]) should coincide. The experimental facts are quite different. The actual blue shift solvent-order can be rationalized, however, on the basis of dipole–dipole interactions, with hydrogen bonding stabilization of the ground state superimposed in the cases of methanol and water.

Two other points deserve comment. The order of increasing blue shift in methanol (relative to acetonitrile) is the same as the order of increasing base strength. Evidently the differences in the base strengths of these amines are smaller in the excited states than in the ground states. Also, the oscillator strengths of the bands of all the compounds except IVc are decreased in methanol. Since hydrogen bonding to the nitrogen doubtless decreases its resonance interaction with the aromatic ring, a decreased intensity is to be expected. The anomaly of IVc may be rationalized on the grounds of relative basicities. Since IVc is the weakest base of all, the specific hydrogen bonding effects might be expected to be proportionately less important; purely polar effects might indeed dominate, and we already have shown that polar effects do not diminish the spectral intensities.

Acknowledgment.—The availability of the n.m.r. spectrometer used in this work was made possible by a grant (CY-5528) from the Public Health Service.

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[31] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[32] G. C. Pimentel, *J. Am. Chem. Soc.*, **79**, 3323 (1957).

[33] H. E. Ungnade, *ibid.*, **75**, 432 (1953).

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LCAO MO Theory of an Organic Biradical with a Probable Triplet Ground State[1a]

BY DAVID KEARNS AND S. EHRENSON[1b]

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The triphenylmethyl derivative biradical recently prepared by Yang and Castro[1c] is predicted by LCAO MO calculations to have a triplet ground state. Preliminary measurements of the paramagnetic susceptibility (3.1×10^{-3} cm.^{3}/mole) and the observation, following the theoretical prediction, of a long wave length absorption peak (beyond 1μ) seem to support this conclusion.

Introduction

Yang and Castro[1c] recently reported the synthesis of a molecule whose structure is shown in Fig. 1. A number of classical resonance structures may be written for this molecule, but, neglecting ionic structures, there are always at least two carbon or oxygen atoms which must have a deficiency of valence bonds. Potentially interesting properties are suggested for this molecule as a result of this deficiency. In this paper we detail a number of these properties and give the results of our approximate theoretical calculations in comparison with some recently obtained experimental results.

Longuet-Higgins[2] has given a proof based on LCAO MO theory for alternant hydrocarbons which states that a molecule will have at least as

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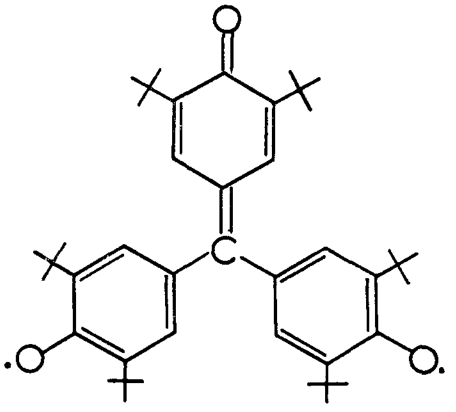
[1] (a) This work was partially supported by the AF Office of Scientific Research of the Air Research and Development Command under contract No. AF49(638)-923. (b) Laboratory of Molecular Structure and Spectra. (c) N. C. Yang and A. J. Castro, *J. Am. Chem. Soc.*, **82**, 6208 (1960).

[2] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).



I

Fig. 1.—Yang and Castro's [1c] organic biradical I.

many unpaired electrons in its ground state as there are atoms which have deficiencies of valence bonds in the principal resonance structures. If we neglect for the moment the possible complications arising from replacement of carbon by oxygen atoms, the above considerations would lead us to expect molecule I to have at least two unpaired electrons in the ground state. Since the unpaired electrons in this molecule are in no obvious way isolated from each other as in other common organic biradicals,[3] it would appear that the ground state should be a triplet.

The proof of the Longuet-Higgins unpaired electron theorem does not depend upon the neglect of overlap or upon the assumption of a constant carbon–carbon resonance integral as long as the molecular symmetry is maintained. We therefore may carry this theorem over in these respects to a consideration of molecules of the type (I). However, the effect of non-constant Coulomb integrals which must be introduced if hetero-atoms are present in the molecule was not considered in the proof of this theorem. Whether the use of a realistic Coulomb integral for the oxygen atoms different from that of carbon could change the alternant-hydrocarbon-based triplet state prediction was a question of interest. We have carried out LCAO MO calculations to investigate this question in some detail; a by-product of the calculations will be the prediction of the absorption spectrum of this molecule which will be compared to the measured spectrum.

Outline of the Calculations.—We have restricted ourselves to the general π-electron framework for systems of the type shown in Fig. 1, *i.e.*, we have neglected any electronic effects of the substituent *t*-butyl groups. The choices of the Coulomb (α), resonance (β) and overlap (S) integrals were based on considerations described below. These integral parameter values were provided as input to a Schmidt-orthogonalization, Jacobi-diagonalization matrix routine written for the Remington Rand 1103A computer.[4] Eigenvalue and vector solutions for the Wheland–Mulliken LCAO MO method[5] were computed for the order 22 matrix in approximately 3 minutes.

Parameter Choices.—The molecule was taken to have a D_3 symmetric propeller shape with rings out of plane by 30°, the same degree of twist used by Adam and Weissman[6] in their treatment of the triphenyl methyl radical. (Although the angle of twist may be somewhat greater due to steric effects of the bulky *t*-butyl groups this should not alter our general conclusions.) A resonance integral of $0.85\beta^0$ was therefore used for the central carbon atom to ring bonds. Nearest neighbor interactions in the rings were assigned unit values of β^0 as were those of carbon with oxygen. Our decision for the latter was based on the moderately successful calculations of similar nature made on benzoquinones employing this approximation.[7] Following the usual approximation the overlap integral S was assumed proportional to β.[8] S^0 was taken as 0.25.

As mentioned above, the choice of a Coulomb integral for the oxygen atoms is the most crucial one. Calculations have been made by others with a variety of values ranging from 0.7 to on the order of $1.3\beta^0$ greater than those for sp^2 carbon.[7,9] As a result, we decided to take an extreme value for these Coulomb integrals corresponding to strong oxygen electronegativity. An α_o value of $\alpha_c + 1.5\beta^0$ was chosen. As the other limit we also computed the Hückel alternant hydrocarbon approximation to this molecule (which assigns the same α value to carbon and oxygen). Further information may be derived from these limiting results by perturbation methods; these will be considered below.

Results and Discussion

Theory A. Nature of the Ground State.—The calculated MO energy level diagrams are given in Fig. 2 where the orbital energies are in units of β^0 relative to α_c taken as the zero of energy. The symmetries of the MO's under D_3 also are indicated in this figure.

Molecule I has 22 π-electrons to be accommodated in these levels. It is apparent from both approximations that the lowest energy state is one where the two highest lying electrons occupy two degenerate orbitals (bonding by $0.542\beta^0$ in the more sophisticated treatment or non-bonding in the alternant hydrocarbon approximation). It should be pointed out that this degeneracy is a group theoretical one and remains as long as the molecule retains D_3 symmetry. Also of importance is the apparent fact that these degenerate orbitals retain their relative energy positions, *i.e.*, between 10 bonding and 10 anti-bonding orbitals, over the limits of our parameter choices.

This latter conclusion may in fact be strengthened beyond what examination of the limiting cases reveals through the use of the Coulson–Longuet-Higgins[10] perturbation relation between orbital energy and Coulomb integral changes. To the first order

$$\delta\epsilon_k = \sum_m C_{mk}{}^2\delta\alpha_m$$

where ϵ_k and C_{mk} are, respectively, the energy of the k-th MO and the AO coefficient of atom m. For the 0.542, 0.800 and $0.827\beta^0$ levels, the values of $\delta\epsilon_k/\delta\alpha_o$ are, respectively, 0.1871, 0 and 0.1753. To this approximation therefore an α_o of at least $\alpha_c + 3\beta^0$ would be required to have

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[3] G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 813.

[4] Computation carried out at Wright Air Force Development, Dayton, Ohio. A more detailed description of this computational method may be found in S. Ehrenson, *J. Am. Chem. Soc.*, **83**, 4493 (1961).

[5] *Cf.*, G. W. Wheland, *ibid.*, **64**, 900 (1942); R. S. Mulliken and C. A. Rieke, *ibid.*, **63**, 1770 (1941).

[6] F. C. Adam and S. I. Weissman, *ibid.*, **80**, 2057 (1958).

[7] A. Kuboyama, *Bull. Chem. Soc. Japan*, **33**, 917 (1960); T. Anno, I. Matubara and A. Sado, *ibid.*, **30**, 168 (1957).

[8] R. S. Mulliken, *J. Chem. Phys.*, **46**, 675 (1949), section 28.

[9] *Cf.*, A. Streitweiser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

[10] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947).

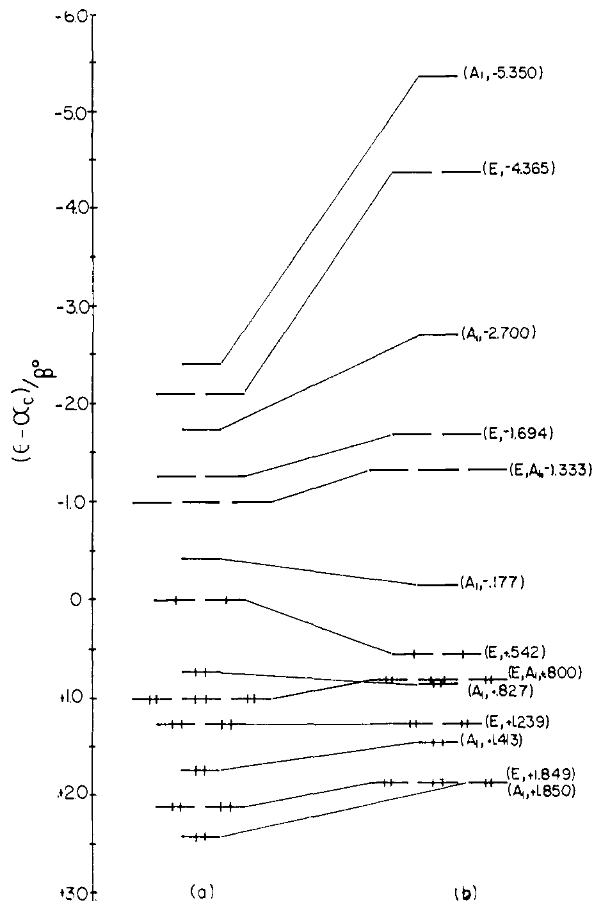

Fig. 2.—Calculated molecular orbital energy levels in (a) Hückel approximation and (b) Wheland–Mulliken approximation.

any of the given levels cross (0.542 and 0.800 for this value)[11]; to cause such a crossing as to make the eleventh least stable MO non-degenerate is virtually precluded. Therefore, according to Hund's rule, the state of lowest energy for this molecule would seem to be one in which each of the degenerate $0.542\beta^0$ levels is singly occupied and the spins of the occupying electrons are paired parallel. This constitutes a triplet ground state.[12]

B. Absorption Spectrum.—The energies and probabilities of the π-electronic transitions of molecule I may be computed within the theoretical approximations employed as follows. The transition energies are simply taken as the differences between the occupied and the unoccupied Wheland–Mulliken type MO's of Fig. 2 with $\beta^0 = -2.0$ ev. Corresponding oscillator strengths f may be computed for these transitions ($\psi_i \rightarrow \psi_k$) by the method of Mulliken and Rieke[13]

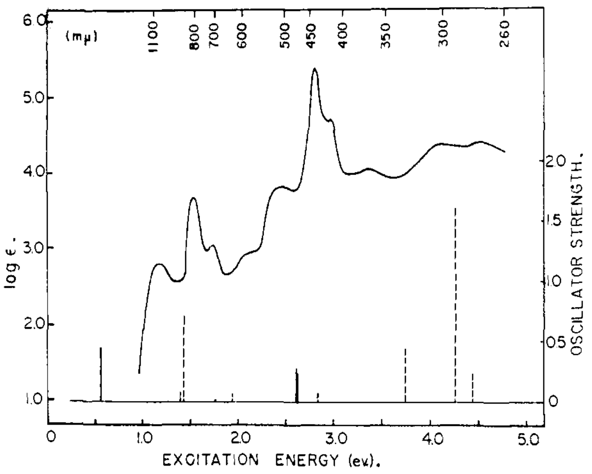

Fig. 3.—Absorption spectrum of biradical I measured in benzene. The vertical lines under the absorption curves give the spectrum predicted when a $\beta^0 = -2.0$ e.v. is used. The solid lines refer to electronic transitions to the $0.542\ \beta^0$ bonding level. The dashed lines refer to transitions to antibonding levels.

$$f = 1.085 \times 10^{11}\, \nu \left(\sqrt{2} \sum_{m} C_{mi} C_{mk}\, \vec{r}_m\right)^2$$

Here, ν is the frequency in cm.$^{-1}$, $\vec{r}_m$ is the position vector of the m-th atom in some convenient coordinate system (units of cm.), and the C's are the MO coefficients. The computed energies are plotted on the ordinate in the lower half of Fig. 3; the abscissa heights are the f values.

Experimental Results

A. Magnetic Susceptibility.—If there were two electrons per molecule with their spin vectors randomly oriented with respect to each other the paramagnetic susceptibility would be expected to be 2.5×10^{-3} cm.^{3}/mole, but if every molecule were in a triplet state the susceptibility should be 3.4×10^{-3}. Preliminary measurements of the bulk susceptibility give a value of 3.1×10^{-3} cm.^{3}/mole for the paramagnetic contribution after the diamagnetic contribution to the susceptibility ($\sim -0.4 \times 10^{-3}$ cm.^{3}/mole)[14] has been subtracted. Unfortunately there is probably sufficient experimental error in these initial measurements to preclude a decision on whether the molecule is triplet or a biradical. At the same time, it seems rather conclusive that it must be one of these.

We may argue that there is no obvious mechanism for isolation of these electrons contributing to the paramagnetic properties of the molecule without the sacrifice of stabilization energy; *i.e.*, twisting one ring perpendicular to the other two rings would allow separation of the electrons but at the same time decrease the stability of the molecule as compared to the structure we have assumed. On this basis it seems very likely that the ground state of molecule I is a triplet; however, more conclusive arguments must await more accurate susceptibility and electron spin resonance measurements.

B. Absorption Spectrum.—The absorption spectrum of molecule I measured in benzene between 2,600 and 26,000 Å. is shown in the top half of Fig. 3. The extent of the agreement between the predicted (lower half of this figure) and the observed energies is uncertain because of the unusually large number of predicted and observed electronic transitions in the visible and near ultraviolet region, coupled of course with the approximate nature of the calculations. From a naïve point of view the agreement seems reasonable. The calculated oscillator strengths and observed intensities

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[11] Interestingly enough this would not change the triplet state prediction since now the three shifted $0.800\beta^0$ levels hold four electrons.

[12] The Jahn–Teller effect is expected to split these degenerate partially filled levels but only by an amount on the order of 0.02 e.v. if comparisons with theoretical estimates for this effect in ions of benzene (0.05) and triphenylene (0.02) are reasonable (*cf.* W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.*, **33**, 1695 (1960)). This splitting, which should be energetically much smaller than the singlet–triplet separation, will in no way alter our triplet ground state conclusions.

[13] R. S. Mulliken and C. A. Rieke, *Repts. Prog. Phys.*, **8**, 231 (1941).

[14] Obtained by summing the atom parameters of Pascal, *cf.* P. W. Selwood, "Magneto-Chemistry," Interscience Publ. Inc., New York, N. Y., 1943, p. 52.

correlate less satisfactorily, however. This is not unexpected in light of the uncertainties pointed out for the energies above and the fact that wave functions are generally an order of magnitude less reliable than energies.

Probably the most significant feature of these results is the predicted transition at very long wave lengths (~ 20,000 Å.). This transition between the levels 0.827 and $0.542\beta^0$ was revealed by the calculations to have an appreciable oscillator strength (~0.4) and therefore likely to be observed before it was experimentally found. This prediction led to an extension of the previously obtained spectrum beyond the visible region, with the result that the peak at 10,500 Å. then was observed. Because small changes in the energies of the levels involved in this transition would result in large percentage changes in the predicted energy of this transition, the predicted and observed position of this long wave length transition may be taken to be in satisfactory agreement. A noteworthy aspect of this transition is that it is predicted to be from a bonding level ($0.827\beta^0$) to the partially filled and also *bonding* degenerate levels ($0.542\beta^0$) containing the molecules' two unpaired electrons. The possibility that the peak at 10,500Å. is due to some overtone of an infrared transition (*e.g.*, from a vibration) with a fundamental further into the infrared, rather than an electronic transition, is rather unlikely when the extinction coefficient (~10^3) is considered. The fact that no other transitions are observed in the spectrum beyond this point out to 26,000 Å. also would argue against this supposition.[15]

Conclusions.—The experimental results obtained to date appear satisfactorily consistent with the theoretical prediction of a triplet ground state for molecule I. Further work on the measurements of unpaired-spin-induced properties is suggested, however. In addition to the susceptibility and spin resonance techniques which should provide useful information, attention to the ultraviolet spectra of this molecule also would seem worthwhile. One might expect to observe phosphorescent emission arising from transitions from a metastable *singlet* state (probably short lived) to the ground triplet state. If such a transition is different only in this inversion of states from other molecules of similar size, the transition energy would be on the order 0.2–0.6 e.v. The possibility of photo-deparamagnetism in contrast to the usual photo-paramagnetism would be another property worth investigating.

Chemical reactivity studies of this molecule also should prove of interest. For example, competition reactions among olefins might provide complementary information on the biradical-triplet question, still to be unambiguously settled.

Acknowledgments.—We are indebted to Prof. N. C. Yang and Mr. Castro for samples of molecule I and for their aid in carrying out the spectral measurements and to Mr. J. P. Bromberg for carrying out the susceptibility measurements.

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[15] A referee has pointed out the possible relation of the 800 mμ transition found here to the shorter wave length transitions observed for the triphenylmethane dyes (~600 mμ); *cf.*, L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **67**, 1212 (1945). The differences in transition energies are likely due mainly to the formal positive charges of the latter singlet ground state molecules and differences in the ring to substituent group resonance integrals.