of the spectral properties of the phenyl halides. The necessary δ's are in the order which would be expected from consideration of ionization potentials, and the δ_I's in turn bear a reasonable relation to these δ's. One also concludes from these studies that while the frequency is primarily a resonance effect, the intensity of these compounds is due primarily to an inductive effect.

Summary

Vapor and solution near ultraviolet absorption spectra of the phenyl halides are presented.

The position and intensity are calculated by crude molecular orbital theory in which allowance has been made for the inductive effect.

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[Contribution from the Departments of Chemistry and Physics, The University of Texas]

Molecular Orbital Theory and Spectra of Monosubstituted Benzenes. V. Styrene, Phenylacetylene and Phenylcyclopropane

By J. F. Music[1] and F. A. Matsen

Molecular orbital theory[2] has been shown to provide a reasonably satisfactory description of the near-ultraviolet absorption of monosubstituted benzenes having a substituent with two unshared $p\pi$ electrons on the α-atom. It is the purpose of this paper to extend the treatment to monosubstituted benzenes with hydrocarbon substituents possessing unsaturation, in particular, styrene, phenylacetylene and phenylcyclopropane.

Outline of the Calculations

The Secular Equation.—The MO's may be constructed from linear combinations of the atomic $2p\pi$ functions, ϕ, on each atom

$$\chi_j = \sum_{i=1}^{n} C_{ji}\phi_i \qquad (1)$$

However, for convenience in the solution of the secular equation, the MO's will be taken as linear combinations of functions which are themselves made up of the ϕ's

$$\chi_j = \sum_{i=1}^{8} \lambda_{ji}\,\psi_i \qquad (2)$$

Here ψ_1 through ψ_6 are orthogonal benzene functions[2] and ψ_7 and ψ_8 are substituent functions which are orthogonal to each other and will be particularized for a given molecule.

Variation treatment and the usual assumptions[2] lead to a secular equation in terms of α and β, which are defined as

$$\alpha = \int \phi_i H \phi_i \,d\tau$$
$$\beta = \int \phi_i H \phi_j \,d\tau$$

for atom i adjacent to j—otherwise taken as zero. The elements of the secular equation are of the form

$$H_{pp} = \alpha + n_i\beta_p$$
$$H_{ss} = \alpha + n_i\beta_s$$
$$H_{ps} = N_i\,\beta_{ps}$$

Here p indexes a phenyl ring function and s, a substituent function. The symbol n_i is a positive or negative integer. After the substitution which follows, the n_i's are seen to be the eigenvalues of the zero order problem for benzene and the substituent. For the benzene levels $n_1 = +2$, $n_2 = n_3 = +1$, $n_4 = n_5 = -1$ and $n_6 = -2$. The quantity N_i is the product of the normalization factors and the coefficients of ϕ_1 and ϕ_7 in ψ_s and ψ_p and will be evaluated for the particular molecule.

These elements of the secular equation can be brought into a simpler form on division by β_p and by making the following substitutions

$$A = \frac{\alpha - E}{\beta_p},\ \gamma_1 = \frac{\beta_{ps}}{\beta_p} \text{ and } \gamma_2 = \frac{\beta_s}{\beta_p}$$

The secular equation factors into a second and a sixth order equation. The second order block has roots $A = \pm 1$ and is independent of the substituent. The sixth order block follows

$$\begin{array}{c|cccccc|}
 & (1) & (3) & (5) & (6) & (7) & (8) \\
(1) & A + 2 & 0 & 0 & 0 & B & C \\
(3) & 0 & A + 1 & 0 & 0 & D & E \\
(5) & 0 & 0 & A - 1 & 0 & D & E \\
(6) & 0 & 0 & 0 & A - 2 & B & C \\
(7) & B & D & D & B & A + n_7\gamma_2 & 0 \\
(8) & C & E & E & C & 0 & A + n_8\gamma_2
\end{array} = 0 \qquad (3)$$

The numbers in parentheses indicate the functions from which the term at the intersection arises. Thus

$$B = \frac{H_{17}}{\beta_p} = \frac{H_{71}}{\beta_p} = \frac{H_{67}}{\beta_p} = \frac{H_{76}}{\beta_p} = N_i\gamma_1$$

Corresponding definitions obtain for C, D and E. This block yields the equation

$$\begin{aligned}
&(A^2 - 1)(A^2 - 4)(A + n_7\gamma_2)(A + n_8\gamma_2) - \\
&\quad 2A(A^2 - 1)[C^2(A + n_7\gamma_2) + B^2(A + n_8\gamma_2)] - \\
&\quad\quad 2A(A^2 - 4)[D^2(A + n_8\gamma_2) + E^2(A + n_7\gamma_2)] + \\
&\quad\quad\quad 4A^2[D^2C^2 - B^2E^2] - 8BCDEA^2 = 0 \qquad (4)
\end{aligned}$$

In equation (4) all constants except the γ_i may be evaluated from specified ψ's.

Evaluation of γ_i.—It may be assumed that the resonance integral, β, is proportional to the over-

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[1] du Pont Fellow, The University of Texas, 1949–1950.

[2] Matsen, This Journal, 72, 5243 (1950).

lap integral, S, which is a function of distance.[3,4] Then, $\gamma = \beta/\beta_p = S/S_p$. By using the overlap integrals for $S(2p\pi, 2p\pi)$ calculated by Mulliken and co-workers[5] only the bond distances need be determined to evaluate γ_i. For the more complicated molecules, the distances are not known. Further, it is attractive to set up a calculation scheme such that a minimum of experimental parameters is needed. The excellent agreement that has been obtained between bond order and distance[6] suggests the use of the calculated bond order instead of the experimentally determined bond distance.

For this purpose, an overlap integral–bond order curve is constructed by assigning a mobile bond order of two to the overlap integral for 1.20 Å., the carbon–carbon distance in acetylene, and similarly for ethylene, benzene and ethane with bond orders of one, two-thirds and zero, respectively (see Fig. 1).

The procedure is first to assume all γ_i equal to unity. This allows solution of the secular equation and yields a set of coefficients. Then the bond orders may be calculated according to the formulation of Coulson[7] $p_{rs} = 2\Sigma C_{jr}C_{js}$. Here C_{jr} is the coefficient of the atomic orbital on atom r in the jth molecular orbital. The summation extends over the occupied orbitals.

The overlap integrals corresponding to these bond orders are read off the curve, and the ratio of the overlap integral of a particular bond to the overlap integral for the average bond[8] in the phenyl group determines γ_i. This may be used to calculate the energy levels and, subsequently, the position of the spectrum.

Position of the Spectrum.—The structure of the near ultraviolet absorption spectra of the compounds (see 0–0 bands listed in Table I) has been analyzed[9] and found to resemble the corresponding spectra of other monosubstituted benzenes. The spectra are taken as arising from the analog of the A_{1g}–B_{2u} transition in benzene. For such a transition, the excited state is the lower of two states resulting from the mixing and splitting of the zero order degenerate states $\chi_3\chi_4$ and $\chi_2\chi_5$.[10]

TABLE I

	Frequency 0–0 bond,[4] cm.$^{-1}$	$(\nu_B - \nu)/\nu_B$ Calcd.	$(\nu_B - \nu)/\nu_B$ Obsd.
Styrene	34,761	0.14	0.087
Phenylacetylene	36,370	.093	.045
Phenylcyclopropane	36,861	.094	.032

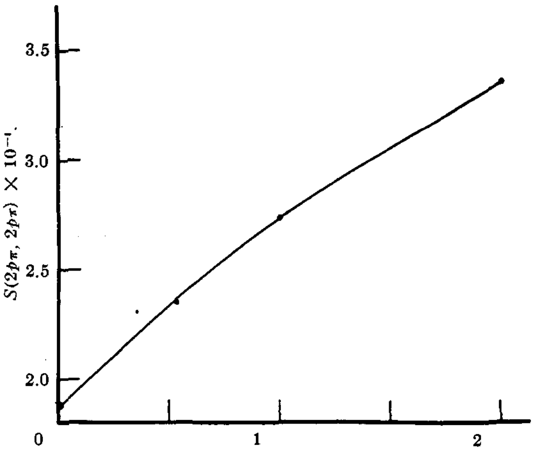

Fig. 1.—Variation of mobile bond order with $S(2p\pi, 2p\pi)$.

The position of the absorption relative to that of benzene may be calculated with either of two assumptions, both of which lead to the same result. First, one may assume that the height of the center of gravity of the excited states above the ground state is given by the average of the individual excitation energies $1/2\ [(E_5 + E_4) - (E_3 + E_2)]$. For benzene this quantity is $-2\beta_p$. Further, it is assumed that on perturbation of the benzene levels by a substituent, the lowest singlet excited state is shifted to the same extent as the center of gravity. These considerations lead to

$$\frac{\nu_B - \nu}{\nu_B} = \frac{1}{4}\{4 + [(A_3 + A_2) - (A_5 + A_4)]\} \quad (5)$$

Here ν_B and ν are the frequencies of the 0–0 band in benzene and the substituted benzenes, respectively.

The second assumption makes no reference to the center of gravity of the four excited states, but is concerned with the nature of those excited states involved in the A_{1g}–B_{2u} type transition. The zero order excitation energy to the state $(1/\sqrt{2})(\chi_3\chi_4 + \chi_2\chi_5)$ is $-2\beta_p$ for benzene and $E_5 - E_2 = E_4 - E_3$ for styrene. Inclusion of electron repulsion will lower the excitation energy of these states for both benzene and styrene. Since the styrene excitation is largely localized in the phenyl group, it will be assumed that the state in each molecule is lowered in energy to the same extent by the electron interaction. Thus

$$\frac{\nu_B - \nu}{\nu_B} = \frac{1}{4}[2 - (A_5 - A_3)]$$

and since $A_4 = -A_2 = 1$ this is identical to (5).

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[3] Wheland, THIS JOURNAL, **64**, 900 (1942).

[4] Van Dranen and Ketelaar, *J. Chem. Phys.*, **17**, 1338 (1949).

[5] Mulliken, Rieke, Orloff and Orloff, *ibid.*, **17**, 1248 (1949).

[6] *Cf.* Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 110.

[7] Coulson, *Proc. Roy. Soc. (London)*, **158A**, 169 (1939).

[8] The bond distances in the phenyl group do not change markedly from compound to compound so that the distance 1.39 Å. can be used to determine the overlap integral for the phenyl group bonds in all compounds. However, for consistency, bond orders will be used. The average bond order will determine the overlap integral for the average bond in the phenyl group.

[9] Robertson, Music and Matsen, THIS JOURNAL, **72**, 5260 (1950).

[10] The states $\chi_3\chi_4$ and $\chi_2\chi_5$ are mainly localized in the ring because χ_3 and χ_4 are exclusively benzene orbitals. The mixing and resultant splitting arises from the electron interaction which is not included in one electron molecular orbital theory. It is of interest to note that this splitting would be expected to push the B_{2u} type state below $\chi_2\chi_5$.

Similar considerations obtain for phenylacetylene and less exactly for the spectrum of phenylcyclopropane.

The Compounds

Styrene.—The ethylenic group carries a 2pπ orbital on each carbon atom, ϕ_7 and ϕ_8. The symmetry orbitals are

$$\chi_7 = \frac{1}{\sqrt{2}}(\phi_7 + \phi_8)$$

$$\chi_8 = \frac{1}{\sqrt{2}}(\phi_7 - \phi_8)$$

Then, $n_7 = +1$, $n_8 = -1$, $B = C = \frac{1}{2\sqrt{3}}\gamma_1$, and $D = E = \frac{1}{\sqrt{6}}\gamma_1$. Setting $\gamma_1 = \gamma_2 = 1$, equation (4) becomes

$$A^6 - 7A^4 + 12A^2 = 4$$

with roots $A_1 = -2.136$, $A_3 = -0.662$, $A_5 = +0.662$, $A_6 = +2.136$, $A_7 = -1.414$, and $A_8 = +1.414$. The mobile bond orders are then $p_{78} = 0.912$, $p_{17} = 0.409$, $p_{12} = p_{16} = 0.614$, $p_{23} = p_{56} = 0.680$ and $p_{34} = p_{45} = 0.659$. These are in agreement with the values obtained by Coulson and Longuet-Higgins.[11] A mean value of 0.65 will be taken for the bond orders in the phenyl group. From Fig. 1, $S_p = 0.247$, $S_{17} = 0.225$ and $S_{78} = 0.267$, then $\gamma_1 = 0.911$ and $\gamma_2 = 1.081$. The second approximations to the energies are $A_1 = -2.116$, $A_3 = -0.723$, $A_5 = +0.723$, $A_6 = +2.116$, $A_7 = -1.414$, $A_8 = +1.414$. The quantity $\frac{\nu_B - \nu}{\nu_B}$ is given in Table I.

Phenylacetylene.—Each carbon atom in the acetylenic group has a pair of mutually perpendicular pπ orbitals. The axes of these orbitals lie in two mutually perpendicular planes which intersect at the figure axis. Only one such plane can be oriented parallel to the axes of the pπ orbitals in the phenyl ring at any one time, and only the set in this plane can interact strongly with the ring orbitals. Since the other set does not interact with the ring, its only effect is to contribute to the bond order of the acetylenic linkage. In conformity with the earlier discussion, this bond order contribution is taken to be one.

In the first approximately all γ_i are taken as unity; so the first stage of the phenylacetylene calculation is identical to that of styrene. For the second stage, the bond orders are the same as in the styrene except that the quantity one is added to the bond order between atoms seven and eight. This makes $\gamma_2 = 1.344$ and ultimately yields the following energy levels: $A_1 = -2.147$, $A_3 = -0.814$, $A_5 = +0.814$, $A_6 = +2.147$, $A_7 = -1.538$, $A_8 = +1.538$. The quantity $(\nu_B - \nu)/\nu_B$ is given in Table I.

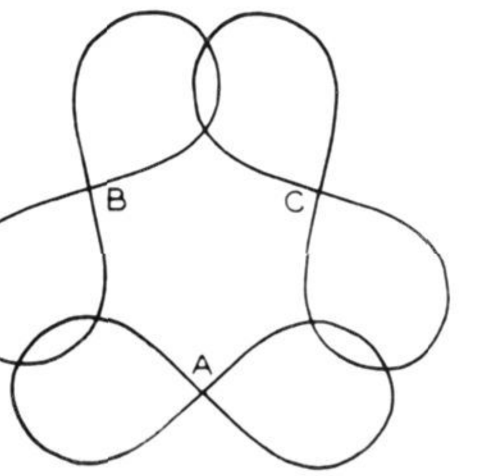

Fig. 2.—The *p* orbitals in the Sugden model of cyclopropane. The carbon atoms are located at A, B and C.

Phenylcyclopropane.—A large quantity of evidence has accumulated[12] which shows that the cyclopropyl group is, to some extent, unsaturated. Sugden[13] has proposed the following model for cyclopropane: It is assumed that, of the four orbitals on a carbon atom, three form sp^2 hybrids whose axes lie on a plane and make angles of 120° with each other. The fourth, an unhybridized pπ orbital, has its axis perpendicular to those of the three hybrid orbitals. Two of the hybrids are bonded to hydrogen atoms which lie on either side of the plane formed by the three carbon atoms. The axes of the third, or "carbon bonded" hybrid orbital, and of the pπ orbital lie in the plane of the carbon atoms (see Fig. 2). The three carbon bonded hybrids, one from each carbon atom, form a set of wave functions which, to the first approximation, is independent of all other atomic orbitals.

The three unhybridized pπ orbitals form a second independent set, and it is this set which confers the unsaturation properties to the molecule. The symmetry orbitals of such a trigonal set are

$$\psi_7 = 1/\sqrt{3}\,(\phi_a + \phi_b + \phi_c)$$

$$\psi_8 = 1/\sqrt{6}\,(2\phi_a - \phi_b - \phi_c)$$

$$\psi_9 = 1/\sqrt{2}\,(\phi_b - \phi_c)$$

Then $n_7 = -2$ and $n_8 = n_9 = +1$. The signs are opposite to those obtained by straightforward application of the earlier definition of H_{ss} because, here, in the integral β_s the positive lobe of one pπ function overlaps the negative lobe of the adjacent one. The resulting change in sign of β_s is incorporated into the n_i.

If the phenyl group is substituted on atom A of the cyclopropane ring ψ_9 is orthogonal to the benzene functions. Thus, equation (4) holds with $B = 1/3\sqrt{2}\,\gamma_1$, $C = D =$

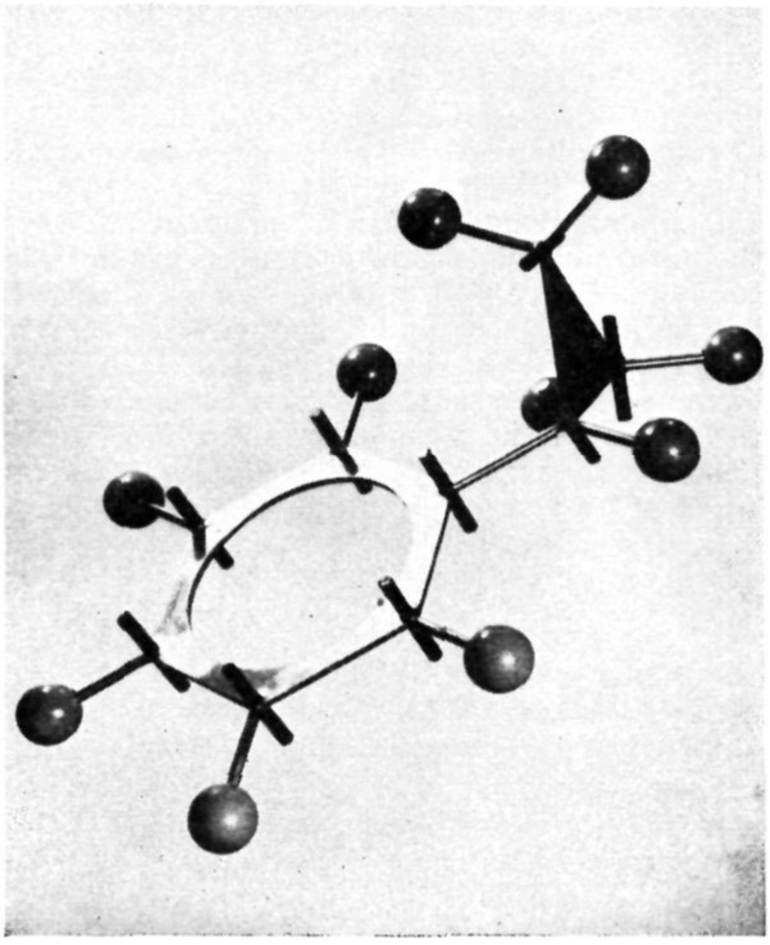

Fig. 3.—Model of phenylcyclopropane. The darker rods, without hydrogen atoms, represent the unhybridized *p* functions.

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[11] Coulson and Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **193A**, 447 (1948); see also Berthier and Pullman, *Compt. rend.*, **228**, 397 (1949).

[12] See the recent review by A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[13] Sugden, *Nature*, **160**, 367 (1947).

$1/3\gamma_1$, $E = \sqrt{2}/3\ \gamma_1$. The resonance integral between atoms one and A is over parallel pπ orbitals just as in styrene and phenylacetylene (see Fig. 3). On the other hand, the resonance integrals in the cyclopropyl group are over pπ functions which make angles of 120° with each other. A computation of the overlap integral for this configuration would give some indication of the magnitude of the corresponding resonance integral. In this paper, however, it will be assumed that the same considerations apply for this integral as for the integral over parallel pπ functions.

Assuming $\gamma_1 = \gamma_2 = 1$ we obtain: $A_1 = -2.154$, $A_3 = -0.593$, $A_5 = +1.000$, $A_6 = +2.348$, $A_7 = -1.447$, $A_8 = +1.845$ with $p_{bc} = 0.688$, $p_{ab} = p_{ac} = 0.611$, $p_{1a} = 0.376$, $p_{12} = p_{16} = 0.618$, $p_{23} = p_{56} = 0.677$, $p_{34} = p_{45} = 0.661$. This yields a new $\gamma_1 = 0.899$, $\gamma_2 = 0.996$[14] and the second approximations to the energies are: $A_1 = -2.120$, $A_3 = -0.625$, $A_5 = +1.000$, $A_6 = +2.298$, $A_7 = -1.408$, $A_8 = +1.852$. The quantity $\frac{(\nu_B - \nu)}{\nu_B}$ is given in Table I.

Intensity

Experimentally the intensity of absorption of the benzene type transition is greater in styrene than in phenylacetylene, which has about the same intensity as phenylcyclopropane.[9] For styrene and phenylacetylene this is the order of the wave lengths of the 0-0 bands, and is in accord with the general observation that the greater the perturbation of the benzene levels by a single substituent, the longer are the wave lengths and the higher is the intensity of absorption.[15]

However, since the one electron states in phenylacetylene and styrene are symmetrically distributed about $A = 0$, the calculated transition probability to the B_{2u} excited state characterized by $\chi_3\chi_4 + \chi_2\chi_5$ (where $\chi_3\chi_4$ stands for the complete wave function containing this factor) is zero just as in benzene.[16] Excitation to the B_{1u} type state characterized by $\chi_2\chi_4 - \chi_3\chi_5$ which is forbidden in benzene, is not forbidden in styrene and phenylacetylene. A calculation of the intensity of this transition gives approximately the observed intensity for both styrene and phenylacetylene. Further study on the intensity is needed.

Discussion

The wave length and bond order calculations indicate that crude MO theory gives a description of properties of certain conjugated hydrocarbons containing the benzene nucleus. Taking the characterization of the phenyl ring as correct, the description of the compound implies a reasonably correct characterization of the substituent.

The fact that phenylacetylene does not absorb at longer wave lengths than does styrene, suggests that not all of the four pπ electrons in the acetylenic group are in interaction with the phenyl group. The familiar acetylenic characterization leads to the conclusion that, at a given time, only one of the two perpendicular sets of mobile electrons can be in maximum alignment with the unsaturation electrons of the ring.

The calculations offer strong support to the Sugden model of cyclopropane. Nothing is implied concerning the uniqueness of the model; but to the extent that this type of calculation characterizes the substituent, the model is satisfactory.

Summary

The position of the near ultraviolet absorption of styrene, phenylacetylene and phenylcyclopropane has been calculated by crude molecular orbital theory and the results compared with experiment.

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[14] Dr. Field and Mr. Hinkle of this Chemistry Department have obtained an ionization energy of cyclopropane of 10.1 e. v. by electron impact. If one assumes the ionization energy to be the energy required to remove an electron from the highest occupied orbital and further that the π electron coulomb integral over carbon has the same value for cyclopropane and ethylene, then βethylene $-$ β cyclopropene $= 10.6 - 10.1 = 0.5$ e. v. Since βethylene ~ 3, βethylene/βcyclopropane ~ 1.2 which should be compared to γethylene/γcyclopropane $= 1.1$.

[15] It may be pointed out that the $A_{1g} - B_{2u}$ type spectrum is considerably weaker in styrene than in phenol and aniline, which lie at approximately the same wave length. Further, phenylacetylene has about the same intensity as phenylcyclopropane, although the former lies at longer wave lengths. The apparent weakness in phenylacetylene and styrene may be a reflection of the forbiddenness which the rough molecular orbital calculations predict as a consequence of the symmetric perturbation of the benzene levels.

[16] An unsymmetrical distribution of energy levels can be obtained by the inclusion of overlap. It can be shown, however, the the inclusion of overlap together with the assumption of proportionality between corresponding resonance and overlap integrals, leaves the form of the secular equation, and, hence, the molecular orbital coefficients unchanged.