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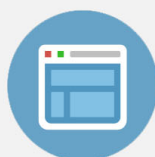
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Molecular Orbital Treatment of the Ultraviolet Spectra of Benzene and Borazole†

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The ground state and the first excited states of benzene and borazole are treated according to the semi-empirical molecular orbital method. Comparing the observed spectra with the computed energies, a spectroscopic value of -2.6 ev for the bond integral β is obtained in the case of benzene. In the case of borazole this procedure includes one more parameter, which takes care of the difference in electronegativity of boron and nitrogen. Taking a reasonable value for this parameter, a value of -2.3 ev for the bond integral between boron and nitrogen, β^* , is obtained in fair agreement with theoretical expectations.

THE benzene molecule has been treated according to the molecular orbital method by Mayer and Sklar.¹ These authors made a completely theoretical computation. For the Hamiltonian, they took for the field of the core the field of six carbon atoms minus six $2p\pi$ electrons, then fed these six electrons into this field and calculated the energies of the ground state and the first excited states. The only empirical value they used was 1.40\AA for the C—C distance.

In the present paper a semi-empirical method is used. The procedure is equally simple for benzene (C_6H_6) and borazole ($\text{B}_3\text{N}_3\text{H}_6$), the only difference being the occurrence of one more parameter in the case of borazole.

Neglecting interactions of non-neighbor ring atoms, we can write the secular equations for the six approximate molecular orbitals, derivable as linear combinations of $2p\pi$ atomic orbitals of the ring atoms, in the form:

$$\begin{vmatrix} A & 1 & 0 & 0 & 0 & 1 \\ 1 & A & 1 & 0 & 0 & 0 \\ 0 & 1 & A & 1 & 0 & 0 \\ 0 & 0 & 1 & A & 1 & 0 \\ 0 & 0 & 0 & 1 & A & 1 \\ 1 & 0 & 0 & 0 & 1 & A \end{vmatrix} = 0 \text{ (benzene),}$$

$$\begin{vmatrix} A' & 1 & 0 & 0 & 0 & 1 \\ 1 & A'' & 1 & 0 & 0 & 0 \\ 0 & 1 & A' & 1 & 0 & 0 \\ 0 & 0 & 1 & A'' & 1 & 0 \\ 0 & 0 & 0 & 1 & A' & 1 \\ 1 & 0 & 0 & 0 & 1 & A'' \end{vmatrix} = 0 \text{ (borazole),}$$

where

$$A = \frac{\alpha - E}{\gamma - S E}, \quad A' = \frac{\alpha' - E}{\gamma^* - S^* E}, \quad A'' = \frac{\alpha'' - E}{\gamma^* - S^* E},$$

$$\alpha = \int \bar{\psi}_C^1 H \psi_C^1 d\tau, \quad \alpha' = \int \bar{\psi}_B^1 H^* \psi_B^1 d\tau,$$

$$\alpha'' = \int \bar{\psi}_N^1 H^* \psi_N^1 d\tau,$$

$$\gamma = \int \bar{\psi}_C^1 H \psi_C^2 d\tau, \quad \gamma^* = \int \bar{\psi}_B^1 H^* \psi_N^2 d\tau,$$

$$S = \int \bar{\psi}_C^1 \psi_C^2 d\tau, \quad S^* = \int \bar{\psi}_B^1 \psi_N^2 d\tau.$$

The ψ 's are atomic $2p\pi$ orbitals, the subscripts referring to the kind of atom, the superscripts to the location in the ring. H and H^* are the one-electron Hartree-field Hamiltonian operators for benzene and borazole, respectively. Substituting

$$\begin{aligned} \alpha - E &= -X, \\ \gamma - S\alpha &= \beta, \\ \gamma^* - S^*\alpha &= \beta^*, \\ \alpha' - \alpha &= \delta', \\ \alpha'' - \alpha &= \delta'', \end{aligned}$$

we get

$$A = \frac{-X}{\beta - SX}, \quad A' = \frac{\delta' - X}{\beta^* - S^*X}, \quad A'' = \frac{\delta'' - X}{\beta^* - S^*X}.$$

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¹ M. G. Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938). See also V. Griffing, J. Chem. Phys. 15, 421 (1947).

The α 's, γ 's, and β 's are known to be negative quantities. The α 's are electronegativity parameters, and can be taken proportional (with reversed sign) to the absolute electronegativities.² In Pauling's electronegativity scale,³ the electronegativity increases by approximately a constant amount for successive members in the second row of the periodic table. We therefore assume $-\delta' = \delta'' = \delta (< 0)$.

By a suitable similarity transformation⁴ the secular equations can be reduced to the forms:

$$\begin{vmatrix} A & 2 & 0 & 0 & 0 & 0 \\ 2 & A & 0 & 0 & 0 & 0 \\ 0 & 0 & A & 1 & 0 & 0 \\ 0 & 0 & 1 & A & 0 & 0 \\ 0 & 0 & 0 & 0 & A & 1 \\ 0 & 0 & 0 & 0 & 1 & A \end{vmatrix} = 0,$$

$$\begin{vmatrix} A' & 2 & 0 & 0 & 0 & 0 \\ 2 & A'' & 0 & 0 & 0 & 0 \\ 0 & 0 & A' & 1 & 0 & 0 \\ 0 & 0 & 1 & A'' & 0 & 0 \\ 0 & 0 & 0 & 0 & A' & 1 \\ 0 & 0 & 0 & 0 & 1 & A'' \end{vmatrix} = 0.$$

(The equation for benzene could be reduced completely by a different transformation based on the higher symmetry of benzene; however, in the given form the similarity between benzene and borazole comes out more clearly.) The molecular orbitals corresponding to the roots $A = -2$ and $A = -1$ (twice), in benzene, or the corresponding orbitals in borazole, are each occupied in the ground state by two electrons. The average height above the ground state of the first group of excited states^{1,5} (three singlets and three triplets), corresponding in benzene to the excitation of one electron from one of the $A = -1$ orbitals to one of the $A = +1$ orbitals, is given by the difference $X_2 - X_1$ of the two roots of

$$A^2 - 1 = 0, \text{ i.e., of } X^2 - (\beta - SX)^2 = 0;$$

² R. S. Mulliken, J. Chem. Phys. 2, 782 (1934); 3, 573 (1935).

³ L. Pauling, *The Nature of the Chemical Bond*, (Cornell University Press, Ithaca, New York, 1940), p. 65.

⁴ These transformations will be treated in a future publication.

⁵ See footnote 12 in J. R. Platt, H. B. Kleven and G. W. Schaeffer, J. Chem. Phys. 15, 598 (1947).

namely

$$X_2 - X_1 = -\frac{2\beta}{1 - S^2}$$

for benzene; and for borazole, of

$$A'A'' - 1 = 0, \text{ i.e. of } X^2 - \delta^2 - (\beta^* - S^*X)^2 = 0;$$

namely

$$X_2 - X_1 = -\frac{2\beta^*}{1 - S^{*2}}(1 + (1 - S^{*2})d^2)^{\frac{1}{2}},$$

where $d = \delta/\beta^* (> 0)$.

The overlap integrals S and S^* can easily be evaluated if we use Slater $2p\pi$ orbitals. The results are:^{6,7}

$$S = \left(1 + x + \frac{2}{5}x^2 + \frac{1}{15}x^3\right)e^{-x}$$

for like atoms, with $x = Z'R/n^*$, where Z' = effective nuclear charge (3.25 for carbon), n^* = effective quantum number (2 for $2p$ orbitals), and R = internuclear distance, in atomic units.

$$S^* = \left\{ \frac{(ab)^{\frac{1}{2}}}{\frac{1}{2}(a+b)} \right\}^{\frac{1}{2}} \frac{1}{\eta^2} \left\{ \cosh \eta x + \frac{1}{\eta} \sinh \eta x \right. \\ \left. + 3 \left(1 - \frac{1}{\eta^2} \right) \frac{1+x}{x^2} \left(\cosh \eta x - \frac{1}{\eta x} \sinh \eta x \right) \right\} e^{-x}$$

for unlike atoms, with

$$a = Z'/n^*, \quad b = Z''/n^*, \quad Z' = 2.60 \text{ for boron,} \\ x = \frac{1}{2}(a+b)R, \quad Z'' = 3.90 \text{ for nitrogen,} \\ \eta = \frac{a-b}{a+b}, \quad n^* = 2.$$

The actual internuclear distances in benzene and borazole are 1.39 Å and 1.44 Å,⁸ respectively. With these values we get $S = 0.25$, $S^* = 0.22$, and for the mean energies from the ground state to the first excited states:

$$\text{benzene: } E_2 - E_1 = -2.13\beta, \\ \text{borazole: } E_2 - E_1 = -2.10\beta^*(1 + 0.952d^2)^{\frac{1}{2}}.$$

As was mentioned above, corresponding to the mean energy E_2 , a group of six electronic states

⁶ Handbuch der Physik, Vol. XXIV, 1, p. 643.

⁷ A. L. Sklar, J. Chem. Phys. 7, 991 (1939).

⁸ S. H. Bauer, J. Am. Chem. Soc. 59, 1804 (1937).

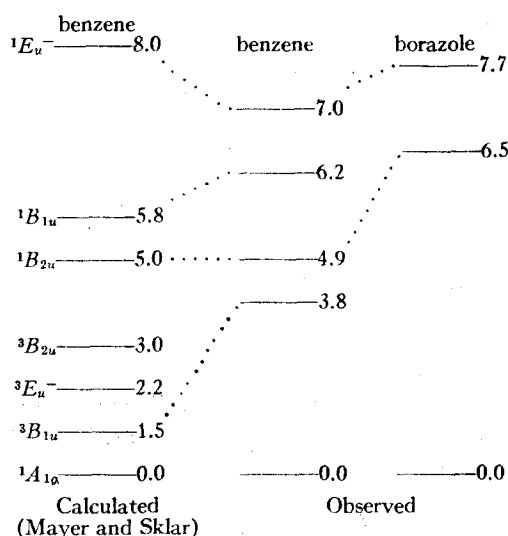


FIG. 1. Calculated and observed electronic energy levels, for vertical excitation (that is, all internuclear distances remaining fixed during the excitation process).

(three triplet and three singlet states) is expected theoretically for each of the two molecules.^{1,5}

In Fig. 1 we give the results of the calculations of Mayer and Sklar on benzene, and the energy levels for benzene and borazole based on observed spectra.⁹⁻¹¹ Since the present calculations apply to vertical excitation, that is, to electron jumps without change in nuclear configuration, the frequencies of the intensity maxima of the band systems in the observed spectra correspond to our energy levels. (For those spectra which were observed in liquid or solution, we have estimated and corrected for the resulting red shift.) The energies above the ground state are given in eV. The group theory notation is essentially that of Placzek and Mulliken, slightly modified by Sponer and Teller.¹²

For transitions from the ground state (1A_g in benzene, $^1A_1'$ in borazole) to the six excited states, group theory gives the following selection rules; corresponding states are listed side by side:

⁹ For benzene: H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, *J. Chem. Phys.* **7**, 207 (1939), where numerous references on experimental data are given; H. Sponer, *J. Chem. Phys.* **8**, 705 (1940).

¹⁰ For borazole: J. R. Platt, H. B. Kleven and G. W. Schaeffer, *J. Chem. Phys.* **15**, 598 (1947).

¹¹ For borazole: L. Jacobs, J. R. Platt, and G. W. Schaeffer, *J. Chem. Phys.* **16**, 116 (1948).

¹² R. S. Mulliken, *Phys. Rev.* **43**, 279 (1933); H. Sponer and E. Teller, *Rev. Mod. Phys.* **13**, 75 (1941); see Table VII.

Benzene Borazole

To 1E_u	$^1E'$	(strongly ¹³) allowed
$^1B_{1u}$	$^1A_1'$	electronically forbidden, but (weakly) allowed in combination with vibrations of species E_g^+ , E' (or B_{2g} , A_2'')
$^1B_{2u}$	$^1A_2'$	electronically forbidden, but (weakly) allowed in combination with vibrations of species E_g^+ , E'
$^3B_{2u}$	$^3A_2'$	electronically and spin forbidden
3E_u	$^3E'$	spin forbidden
$^3B_{1u}$	$^3A_1'$	electronically and spin forbidden

The observed benzene spectrum shows a strong band system at 7.0 eV, two weaker ones at 6.2 and 4.9 eV, and a very weak one at 3.8 eV (the energies given are those for peak absorption in each case). In obtaining these values, besides the liquid or solution correction already mentioned, we subtracted one vibrational quantum of the E_g^+ or E' vibration which made the transitions from the ground state to the B or A' levels allowed.

The 7.0-eV band system is the allowed transition;¹⁴ the 6.2- and 4.9-eV band systems are the transitions to the $^1B_{1u}$ ¹⁴ and $^1B_{2u}$ ^{15,15a} levels, respectively. The identification of the 4.9-eV band system has been thoroughly established by a careful vibrational structure analysis.^{9,15a} The 3.8-eV band system^{15,16} must be interpreted as the transition to the $^3B_{1u}$ ¹⁵ (or the $^3B_{2u}$ ¹⁷) level,

¹³ R. S. Mulliken, *J. Chem. Phys.* **7**, 984 (1939).

¹⁴ The present interpretations of the 6.2- and 4.9-eV systems were first suggested as a possibility by Mayer and Sklar (reference 1). The definite interpretations were first given by G. Nordheim, H. Sponer, and E. Teller, *J. Chem. Phys.* **8**, 455 (1940), as modified by R. S. Mulliken (see footnote 9 in the paper of Nordheim, Sponer, and Teller).

¹⁵ A. L. Sklar, *J. Chem. Phys.* **5**, 669 (1937).

^{15a} The vibrational analysis shows that the 4.9-eV transition is electronically forbidden, and vibrations of symmetry E_g^+ which make the transition allowed, can be indicated. This proves that the electronic level is either $^1B_{1u}$ or $^1B_{2u}$. A transition to a $^1B_{1u}$ level should also be made allowed by a vibration of symmetry B_{2g} ; the presence of such a vibration in the band would establish the symmetry of the electronic level as $^1B_{1u}$ for certain, its absence would make $^1B_{2u}$ probable. A more detailed vibrational analysis of the 4.9-eV band might confirm or disprove the labeling $^1B_{2u}$.

¹⁶ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1945).

¹⁷ From the numerical values of the integrals computed by Mayer and Sklar the $^3B_{1u}$ level should be the lowest, the

since the low intensity in absorption and the long phosphorescence lifetime¹⁸ indicates a doubly forbidden transition, and its appearance in phosphorescence shows that it must be from the lowest triplet level.^{16,19} Since no other band systems have been found in the visible or near ultraviolet, and the transition to the ${}^3E_u^-$ state is expected to be about 10^3 times stronger than the observed singlet-triplet transition, the ${}^3E_u^-$ level must be at least as high as 4.7 eV; the transition to this level could then be masked by the 4.9-eV band system, which is expected to be 10^2 times stronger.²⁰ Since a larger shift is improbable, we shall in estimating the locations of the unobserved levels assume 4.7 eV for the ${}^3E_u^-$ level. For the remaining unobserved ${}^3B_{2u}$ (or ${}^3B_{1u}$) level we shall assume 5.6 eV, since Mayer's and Sklar's calculations give equal separations among the three triplet levels. The fact thus probably established, that the ${}^3B_{2u}$ (or ${}^3B_{1u}$) level must be above the lowest singlet level, means that the calculations of Mayer and Sklar not only give numerical values of some interaction integrals in disagreement with experiment, but even with the wrong sign. However, as these authors pointed out, any orbital type of approximate calculation tends to give triplet states somewhat too low compared to singlet states.

The observed spectrum of borazole, if we accept the interpretation given in reference 11, shows the allowed transition at 7.7 eV, and the equivalent of the 4.9-eV transition in benzene at 6.5 eV. To complete the picture of the energy levels, we assume the splittings of the six levels to be proportional to the splittings in benzene.

${}^3B_{2u}$ level the highest, among the triplet states. However, if the true values of the integrals should be somewhat different, the ${}^3B_{2u}$ might be the lowest, the ${}^3B_{1u}$ the highest. In any event, the theoretical prediction that the ${}^3E_u^-$ should lie in the middle is independent of the numerical values of the integrals.

¹⁸ 4.0 sec. (private communication from M. Kasha). This agrees roughly as to order of magnitude with the lifetime of about 0.1 or 0.2 sec. calculated from the observed absorption. (The absorption f value, estimated from Fig. 13 on p. 1000 of reference 16, is about 1.2×10^{-2} .)

¹⁹ G. N. Lewis and M. Kasha, J. Am. Chem. Soc. 66, 2100 (1944).

²⁰ The transition to ${}^3B_{1u}$ is about 10^{-5} times as strong as that to ${}^3B_{2u}$; since the transition to ${}^3B_{2u}$ is about 10^{-3} times as strong (see J. R. Platt and H. B. Klevens, Chem. Rev. 41, 301 (1947)) as that to ${}^3E_u^-$, we expect the transition to ${}^3E_u^-$ to be about 10^3 times stronger than that to ${}^3B_{1u}$ and thus about 10^2 times weaker than the ${}^3B_{2u}$ transition.

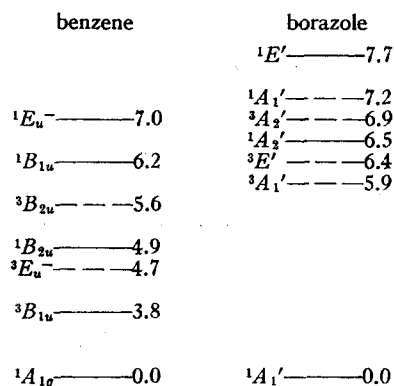


FIG. 2. Observed and (dashed lines) estimated electronic energy levels, for vertical excitation. In benzene it is fairly likely that the labels of the two 3B levels should be interchanged, and similarly for the two 3A levels of borazole. Similar reversals may also be needed for the corresponding singlet levels.^{16a}

The final results for both molecules are shown in Fig. 2.

In the formulas which we derived for the energy difference $E_2 - E_1$ between the first excited states and the ground state in terms of the bond integral β , E_2 refers to the average of the energies of the six levels we have just been discussing (in averaging, each E level must be taken with double weight since these levels are orbitally doubly degenerate; corresponding singlet and triplet levels are, however, given equal weight, a procedure whose correctness can be seen by referring to ref. 1). The resulting averages are 5.5 eV for benzene and 6.8 eV for borazole. (These averages do not depend on a change in labels of the B or A levels.^{15a,17})

The formula then gives for benzene, if we designate by β_{spec} the spectroscopically determined β , $\beta_{\text{spec}} = -5.5/2.13 = -2.6$ eV. From spectroscopic data on ethylene, the value $\beta_{\text{spec}} = -3.0$ eV is obtained,²¹ again for a $2p\pi$ C—C bond although for a somewhat smaller internuclear distance. From resonance energy data another β value can be obtained for benzene:²¹ $\beta_{\text{res}} = -3.1$ eV.

For borazole, we find

$$\beta_{\text{spec}}^* = -6.8/2.1(1.95)^{\frac{1}{2}} = -2.3 \text{ eV} \quad \text{if we assume } d=1.0,$$

²¹ R. S. Mulliken and C. A. Rieke, Rev. Mod. Phys. 14, 259 (A) (1942); and full papers to be published shortly, in which the significance of bond integrals from spectroscopic and other data will be discussed.

or

$$\beta_{\text{spec}}^* = -6.8/2.1(3.14)^{\frac{1}{2}} = -1.8 \text{ ev}$$

if we assume $d = 1.5$.

This gives for δ the respective values -2.3 and -2.7 ev. The first choice gives the closest resemblance between benzene and borazole and

gives at the same time what is probably a reasonable value for δ .²

It can be seen from the formulas for $E_2 - E_1$ that the main reason for the higher frequency of the borazole spectrum as compared with benzene is the appearance of the parameter d in the formula for borazole.

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The Effect of Certain Column Variables on Thermal Diffusion

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(Received October 3, 1947)

Tests have been made on two thermal diffusion columns with different annular spacing. The results indicate that the dependence of the separation on temperature and annular spacing predicted by Furry, Jones, and Onsager holds. The dependence on pressure is slightly different than was predicted. The possibility that the index of repulsive force may depend on the pressure is pointed out.

NOMENCLATURE

- C_v = specific heat at constant volume
- D_{12} = coefficient of ordinary diffusion
- D_T = coefficient of thermal diffusion
- g = gravitational constant
- L = column length
- p = pressure in atmospheres
- q = separation factor $(X_1^T X_2^B / X_2^T X_1^B)$
- T = absolute temperature, °K
- \bar{T} = arithmetic average temperature, °K
- ΔT = temperature difference between hot and cold walls
- v_1, v_2 = convection velocity of species 1, 2
- X_1, X_2 = mole fraction of species 1, 2 in feed
- X_1^T, X_2^T = mole fraction of species 1, 2 in top reservoir
- X_1^B, X_2^B = mole fraction of species 1, 2 in b.t.m. reservoir
- w = one half of annular spacing
- α = thermal diffusion ratio $= (D_T/D_{12})$
- δ, ϵ = empirical constants
- η = viscosity
- λ = thermal conductivity
- ρ = density
- ν = index of repulsive force in $F = -(K_{12}/r^\nu)$

INTRODUCTION

THERMAL diffusion—the transport of molecules caused by a temperature gradient, was predicted theoretically by Enskog¹ in 1911

¹ D. Enskog, *Physik. Zeits.* 12, 56, 533 (1911).

and independently by Chapman² in 1916. Its existence was confirmed experimentally by Chapman and Dootson³ in 1917. With the development of the thermal diffusion column with hot wire by Clusius and Dickel⁴ and the refinement to a concentric tube column by Brewer and Bramley,⁵ it became a practical process for isotope separation.

Furry, Jones, and Onsager⁶ and later Furry and Jones⁷ have presented an extensive analysis of the theory of the column. This paper reviews their results briefly and compares the predicted effect of certain column variables on the separation with experiment.

THEORY

Furry, Jones, and Onsager⁶ use the defining equation:

$$X_1 X_2 (v_1 - v_2) = -D_{12} \text{grad} X_1 + D_T \text{grad} \ln T, \quad (1a)$$

² S. Chapman, *Phil. Trans.* 216A, 279 (1916).

³ S. Chapman and F. W. Dootson, *Phil. Mag.* 38, 248 (1917).

⁴ K. Clusius and G. Dickel, *Naturwiss.* 26, 546 (1938).

⁵ A. K. Brewer and A. Bramley, *Phys. Rev.* 55, 590(A) (1939).

⁶ W. H. Furry, R. C. Jones, and L. Onsager, *Phys. Rev.* 55, 1083 (1939).

⁷ W. H. Furry and R. C. Jones, *Rev. Mod. Phys.* 18, 219 (1946).