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Covalent and Ionic Character in Ground and Excited States of Benzene

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Abstract: Various wave functions for the ground ($^1A_{1g}$) and low-lying excited states of benzene were examined by projecting onto them the valence-bond functions corresponding to Kekulé, Dewar, and Coulomb-stabilized ionic structures. The results show large (75%) contributions from singly ionic structures, 40–50% Kekulé structure for the ground state, and 30–40% covalent character to the $^1B_{2u}$ state. The molecular wave functions are also examined for benzene distorted to a "cyclohexatriene" structure, particularly to determine the relative contributions of the two (now nonequivalent) Kekulé structures. The more favored or short double-bond structure increases its contribution about 25%, and the less favored structure decreases by about the same fraction. The relative change in Kekulé contributions and in corresponding pairs of ionic functions are the most significant changes associated with the distortion.

The quest for usefully accurate molecular wave functions has clearly reached a fruitful plateau. Wave functions now available for diatomic and small polyatomic molecules are sufficiently accurate to permit the calculation of a large variety of the ground-state properties of interest in traditional chemistry. These functions are not only numerically accurate; through the medium of contour maps,[2] they provide us with clear intuitive physical understanding of the variation of wave functions from state to state and from molecule to molecule. The collection of results, taken together, offers a happy rejoinder to the pessimistic reservations that were heard during the earliest years of the computer era.

To add to the information obtainable from orbital and total wave-function contours, we felt that we could gain further insight into molecular behavior from another type of analysis. This analysis, with origins in traditional interpretations of electronic structure, is nevertheless still part of the chemist's vocabulary and is perhaps a meaningful contributor to his chemical intuition. Specifically, we refer to the determination of covalent and ionic character, as represented by valence-bond functions.

The basic idea is this: each valence-bond function represents a kind of physical behavior which we "understand" or can use for the interpretation of chemical behavior. The true molecular wave function Ω or a reasonable approximation of it can be represented by a sum of contributions from a set of valence-bond (VB) functions, or from any complete basis set of functions, according to the principal of superposition. If the set happens to be a set of VB functions, we conventionally call the phenomenon of superposition "resonance." If each function in the basis set is normalized to unity, then the coefficient or amplitude of a function is a measure of its contribution to the exact or approximate function Ω under consideration; specifically, the absolute square of the coefficient of the basis function Ψ_J is the fraction of Ω which is composed of Ψ_J.

We should explain and review just a little more of what the approach does and does not imply. First, it is very important to recognize that valence-bond

(1) (a) Yale University; (b) University of Chicago.
(2) A. C. Wahl, Science, 151, 961 (1966); K. Ruedenberg, private communication.

wave functions are very highly correlated functions, with respect to both space and spin. A valence-bond analysis is not a population analysis in the sense that molecular orbital functions give population analyses; with valence-bond functions one can ask questions like "In a triplet state of benzene, what is the probability that, if one of the unpaired electrons is one atom 1, we will find the other on atom 4, while the remaining π electrons are in 2-3 and 5-6 bonds?" In other words, a valence-bond analysis is a very specific sort of analysis of electron correlation.

Second, we must remember that traditional valence-bond functions are not orthogonal to each other. This mathematical relationship between the functions has its parallel in physical terms; thus, the physical conditions represented by two valence-bond conditions are not in general mutually exclusive conditions. A covalent bond carries some ionic character in the traditional valence-bond representation. This nonorthogonality and the complexity of physical interpretation that accompanies it has two sources. One is the nonorthogonality of the basic atomic orbitals on different atoms; the other, much more bothersome for interpretive purposes, is due to the overcompleteness of the set of valence-bond structures. The first problem can be eliminated by generating a set of orthogonalized atomic orbitals, e.g., equivalent orbitals, and using these as basis functions. One necessarily delocalizes an orbital on one atom when one orthogonalizes it to an orbital on another atom. Consequently this orthogonality is obtained at the expense of a little intuitive understanding, at least insofar as our understanding of valence-bond structures are associated with localized orbitals. The other type of nonorthogonality has been discussed, for example, in connection with the question of resonance in butadiene.[3] It comes from the fact that one can in general draw more structures for a molecule than the number of *independent* functions, just as one can draw more than two vectors on an array of point in a plane. Yet just as any vector on the array can be represented with any two independent (nonparallel) vectors, any of the possible valence-bond structures of a molecule can be expressed in terms of some small number of independent structures. Thus for benzene's π electrons there are twelve possible nonionic singlet VB structures, but only six (any six) are independent. And with this overcompleteness comes the nonorthogonality problem: although we may choose six independent functions, in general these are not orthogonal; if we make them orthogonal, only one function of the orthogonal set can be chosen to represent a single valence-bond structure. We are forced either to give up orthogonality and to make our individual functions easily interpretable, or to make the functions orthogonal and therefore mutually exclusive, but accept basis functions that do not represent single structures.
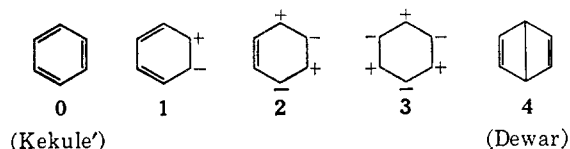
The foregoing discussion is of course simply a review of some of the ramifications of valence-bond methods that have been long recognized in the literature of wave-function calculations. However, it seemed desirable to refresh our memories of some of these ramifications because of the possible misinterpretations which might arise if they are overlooked.

We have selected several representative wave functions for the six π electrons of benzene and projected onto these functions a number of suitably symmetrized valence-bond (VB) structure functions. The squares of these projections are the numbers of interest to us here; the square of the projection of a VB structure function Ψ onto an "accurate" six-electron function Ω, namely, $|(\Omega|\Psi)|^2$, is the fraction of Ω which is made of Ψ. An analysis of this kind could have been performed by calculating the molecular wave function with a VB basis set, but the projection procedure is far more efficient, in view of the availability of rather good wave functions.
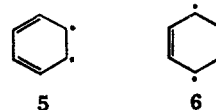
We have chosen to examine the π electrons of benzene for three reasons. First, we wished to find the relative importance of the Kekulé (or better, perhaps, Thiele) structure and of the ionic structures having the greatest Coulomb stabilization. Second, we wanted to learn how these contributions to the ground and low-lying excited states differed. Third, we were interested in the behavior of the electron pairing with molecular vibration, and particularly in the relative contributions of the two Kekulé structures when the bond lengths of the ring alternate between the values appropriate to "pure" double and single bonds.

The first reason was prompted by the results of a similar analysis of ground-state wave functions of butadiene.[3] The butadiene functions were naturally composed of 70-88% of the normal covalent structure, but, surprisingly, contained over 40% of the $C^+C^-C^+C^-$ structure. Such numbers raised questions in our minds of the role of multiply ionized structures in benzene. Craig[4] had actually carried out calculations with a VB basis but had restricted his functions to the Kekulé, Dewar, and singly ionized structures, including ionic Dewar structures. In light of the butadiene results, we chose to evaluate the projections of a somewhat different set, namely, the appropriately symmetrized combinations of structures 0-4. We shall refer to a

| 0 | 1 | 2 | 3 | 4 |

(Kekule')   (Dewar)

VB function representing a single diagram like those of 0-4 as a *primitive* VB function. A linear combination of physically equivalent primitive VB functions which transforms as an irreducible representation of the molecular point group is called a *symmetrized* VB function, or for convenience, simply a VB function.

The second part of this study is a comparison of the VB composition of the $^1A_{1g}$ ground state with various VB contributions to the lower excited states. We have calculated the contributions of structures 0-3 to the $^1B_{1u}$ and $^1B_{2u}$ states, the states responsible for benzene's absorption bands in the 2400- and 2000-A regions. We have also examined briefly the corresponding triplets, looking particularly at the roles of

5   6

(3) R. S. Berry, *J. Chem. Phys.*, 30, 936 (1959).

(4) D. P. Craig, *Proc. Roy. Soc.* (London), A200, 401 (1950).

Table I. Squares of Projections of VB Functions for Benzene in the
$^1A_{1g}$ Ground State in Equilibrium Configuration[a]

VB function onto	Primitive Ψ_0	Symmetrized Ψ_0	Symmetrized Ψ_1	Symmetrized Ψ_2	Symmetrized Ψ_3	Primitive Ψ_4
$^1A_{1g}$-a	0.260	0.395	0.759	0.641	0.225	...
$^1A_{1g}$-b	0.258	0.392	0.757	0.640	0.223	...
$^1A_{1g}$-c	0.437	0.675	0.759	0.328	0.064	0.346

[a] $R_{C-C} = 1.393$ A.

structures **5** and **6**. Note that **6** is the triplet analog of the Dewar structure **4**.

The third part of the analysis was stimulated by the recognition that benzene's normal vibration of b_{2u} symmetry carried the molecule into a geometry appropriate to a cyclohexatriene structure.[5] If the C–C bond distances in a hypothetical "cyclohexatriene" molecule are 1.465 and 1.335 A,[6] then the benzene ring spends roughly 15% of its time distorted enough to reach or pass the cyclohexatriene geometry. The rather obvious next question was this: to what degree do the electrons respond to a cyclohexatriene geometry by correlating themselves according to a *single* Kekulé structure? When the C–C bonds alternate in length between 1.465 and 1.335 A, what are relative contributions of the two Kekulé structures?

Description of the Calculations

Before presenting the results of the analysis, let us describe the "accurate" wave functions we used. The details of the method of calculation are given in Appendix 1. For the $^1A_{1g}$ ground electronic state of the undistorted (D_{6h}) benzene molecule, we used three different functions, denoted by the letters a, b, and c: "a" is a single configuration, based on *atomic* self-consistent field (SCF) orbitals of carbon;[7] "b" is a single configuration, based on Clementi's full molecular SCF calculation for all electrons of benzene,[8] which is probably the best available *uncorrelated* wave function for this molecule; and "c" is the 22-term configuration interaction function of Moskowitz and Barnett based on single Slater function representations of the atomic carbon orbitals.[9] This function does account for electron correlation but suffers from the limitation of the single Slater orbital representation. We shall refer to these three representations of the ground-state function as $^1A_{1g}$-a, $^1A_{1g}$-b, and $^1A_{1g}$-c, respectively. Unfortunately no function is yet available which combines the use of accurate atomic orbitals, as in b, with configuration interaction as in c.

For the excited states we examined the following functions, which we denote simply by the state designation and approximation: for the $^1B_{2u}$ state, all three approximations, $^1B_{2u}$-a (based on atomic SCF orbitals), $^1B_{2u}$-b (based on Clementi's full molecular SCF function), and $^1B_{2u}$-c (Moskowitz' 13-term configuration interaction function for this state); and for the $^1B_{1u}$ state, and the triplets $^3B_{1u}$ and $^3B_{2u}$, only the configuration interaction functions of Moskowitz, *i.e.*, the functions cor-

(5) R. S. Berry, *J. Chem. Phys.*, **35**, 2253 (1961).
(6) C. C. Costain and B. P. Stoicheff, *ibid.*, **30**, 777 (1959); H. J. Bernstein, *Trans. Faraday Soc.*, **57**, 1649 (1961).
(7) R. Silbey, N. R. Kestner, J. Jortner, and S. A. Rice, *J. Chem. Phys.*, **42**, 444 (1965). The ^3P SCF AO set was used.
(8) E. Clementi, private communication.
(9) J. Moskowitz and M. P. Barnett, *J. Chem. Phys.*, **39**, 1557 (1963). The eigenvectors were very kindly supplied by Dr. Moskowitz.

responding to approximation c, which have 16, 13, and 18 molecular orbital configuration basis functions, respectively.

For the distorted molecule, whose symmetry is D_{3h}, we used the $2p\pi$ atomic SCF orbital basis. With these, we carried out a variational calculation to determine a best set of molecular orbitals. Specifically, when the molecular symmetry is reduced from D_{6h} to D_{3h}, the e_g and e_u orbitals all become e'' orbitals (e'' and e''_*) and can mix, in pairs. We therefore replace the lowest configuration with a simple variational function

$$(a_{2u})^2(e_{1g})^4 \underset{D_{6h}}{\longrightarrow} (a''_1)^2(e'' \cos \omega + e''_* \sin \omega)^4 \quad D_{3h}$$

and expand the new function in terms of simple configurations based on e'' and e''_* functions. To find the optimum mixture of the e'' and e''_* orbitals, we need only diagonalize a 2×2 one-electron Hamiltonian (see Appendix 2).

Results

A. Ground State. Table I contains the values of squares of projections onto the ground state of functions representing structures **0–4**. The primitive Dewar structure **4** was done only for the configuration interaction (CI) function $^1A_{1g}$-c; this is of little concern because it was really wanted only for comparison with the triplets. We remind the reader that the VB functions are highly nonorthogonal, so that the sums of the squares of the projections will in general be much larger than unity.

The first two rows of Table I are extremely similar, for a very simple reason. The π-molecular orbitals of D_{6h} benzene are fixed entirely by symmetry, and the composition of these orbitals in terms of VB functions is thereby determined. The only differences between the first row and the second in these two tables arise from the differences in the atomic overlap. The corresponding values for the single Slater function set without configuration interaction were also generated during the computation of the projections onto Moskowitz–Barnett functions. These are also quite similar to the first two rows, but about 10% smaller because of the smaller overlaps of the Slater basis set.

The amount of polar character in the benzene ground state is rather striking. Even after configuration interaction the $^1A_{1g}$ function retains a large portion of its singly ionic structure. The total covalent contribution increases considerably with CI, apparently at the expense of the doubly and especially the triply ionic function. We must exercise a little care in attributing an increase in one function to a decrease in another, both because of the nonorthogonality problem and because we have examined only a few structures. From

the analogy of the butadiene calculation,[3] we may expect the Slater function calculation of Moskowitz and Barnett to *underestimate* the amount of ionic character because of the inherently large estimate of the energy required to form a C^+C^- pair in this basis set.

B. Excited Singlets. Some of the VB structures are naturally excluded by symmetry considerations from contributing to particular excited states. For example, the two Kekulé structures can give only A_{1g} and B_{2u} combinations, and so are excluded from the B_{1u}; the triply ionic structure (3) and its counterpart can give a sum and difference with A_{1g} and B_{1u} symmetry, but no B_{2u}; the Dewar structure (4) cannot contribute B_{2u} either. These relations provided useful checks of the computational machinery.

In Table II we see both an analysis of various functions representing the $^1B_{2u}$, and, in the last line, the CI result alone for the $^1B_{1u}$. The physical situations in these two states are quite strikingly different; the lower energy B_{2u} is almost entirely covalent, while the B_{1u} has considerable doubly and triply ionic character.

Table II. Squares of Projections of VB Functions for Benzene in $^1B_{2u}$ and $^1B_{1u}$ States in Equilibrium Configuration[a]

VB function	Primitive Ψ_0	Symmetrized Ψ_0	Symmetrized Ψ_1	Symmetrized Ψ_2	Symmetrized Ψ_3
$^1B_{2u}$-a	0.149	0.439	0.844	0.520	0
$^1B_{2u}$-b	0.147	0.432	0.840	0.512	0
$^1B_{2u}$-c	0.320	0.907	0.525	0.116	0
$^1B_{1u}$-c	0	0	0.562	0.611	0.215

[a] Equilibrium, that is, for the ground state, with $R = 1.393$ A.

Note that symmetry alone forces the $^1B_{2u}$ function to have a large amount of singly and doubly ionic character, but that CI reduces these considerably. The Moskowitz–Barnett single configuration, not shown in Table III, gives almost 0.8 for the symmetrized Ψ_1, so the reduction is not an artifact of the orbital basis set.

C. Triplet. The triplet result can be described very briefly. Symmetry excludes the nonionic structures 5 and 6 from the next-lowest triplet, the $^1B_{2u}$, but not from the lowest triplet, the $^3B_{1u}$. The primitive function representing structure 5 contributes 26% of the total function $^5B_{1u}$-c, and the Dewar-like or quinoid triplet, 40% of the same function. Recall from Table I that the ground state has 35% of the primitive Dewar structure. We interpret this to mean that the lowest triplet state may have a little more quinoid character than the ground state, but not vastly more.

D. Distorted Benzene. The results in the first line of Table III exhibit an interesting contrast to the first two lines of Table I. Note that it is with the *second* lines of Tables I and II, for $^1A_{1g}$-b and $^1B_{2u}$-b, that the

calculations of Table III should be compared, and not the third lines. No CI function is available for the distorted species, and it was our feeling that our one-parameter variation of the SCF function would give a sufficiently accurate measure of the *relative change* in the contributions of the two Kekulé structures. The total "symmetrized Ψ_0" in column 3 of Table III is based on the projection of the sum of the functions in the first two columns and is the equivalent of a Thiele structure in the same sense as the symmetrized Ψ_0 of Table I. The value of 0.399 is essentially the same as the values of 0.395 for the symmetrized Ψ_0 function on $^1A_{1g}$-a in Table I. However, the primitive Ψ_0 in D_{6h} symmetry gives a value for $|(\Psi_0| \, ^1A_{1g}\text{-a})|^2$ of 0.260; the two corresponding structures in our D_{3h} structure give essentially this average value, but the expected change in the relative contributions of these functions does actually occur. The contributions of the two covalent structures change, one upward and the other downward, by roughly 25%. The change is not startling, but it is very significant. By contrast to the change in the two Kekulé functions, the triply ionic contribution, Ψ_3, does not change dramatically when the C_6 ring is distorted to D_{3h} symmetry. This lack of change is particularly evident in the $^1B_{2u}$ excited state, where triply ionic character is forbidden in sixfold symmetry but allowed in D_{3h}. The actual amount of triply ionic character in $^1B_{2u}$-a, in the D_{3h} form, is only 0.01%, so that the distortion is a very small perturbation so far as "triple-ionization" is concerned.
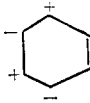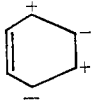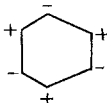
We shall close with a remark about a limitation of a method such as the one used here. The concept of a valence-bond structure is meaningful only in terms of a specific set of atomic orbitals. As such, it can be used to analyze only those wave functions based on a single, well-defined set of atomic orbitals. The method will not be applicable to configuration interaction wave functions based on configurations each of which has its own uniquely determined basis set, chosen for example to make each configuration satisfy self-consistent field and orthogonality relationships.

**Appendix. 1. Method of Computing Projections**

The projections were calculated in this way. Let Ψ represent the set of symmetrized VB spin eigenfunc-

Table III. Squares of Projections of VB Functions onto Distorted[a] (D_{3h}) Benzene. Ground and First-Excited Singlet States

VB function[b]			"Symmetrized Ψ_0" (Thiele)					
$^1A_1{}'$[c]	0.337	0.204	0.399	0.573	0.342	0.481	0.351	0.220
$^1A_1{}'$ from $^1B_2$[d]	0.155	0.138	0.438	0.329	0.386	0.135	0.206	0.0001

[a] Alternating lengths of 1.335 and 1.464 A. [b] All functions taken symmetrized to transform as $A_1{}'$ in D_{3h}. [c] Determined as described in text. [d] Based on orbital parameters found in fixing ground-state function.

Table IV. Sets of Atomic Overlap Integrals

	S_{12}	S_{13}	S_{14}	S_{23}	S_{12}	S_{13}	S_{14}
a (atomic SCF)	0.32155	0.07992	0.04625	0.34565	0.29346	0.07847	0.04525
b (Clementi)	0.31009	0.05796	0.02674				
c (Moskowitz)	0.24850	0.03519	0.01571				

tions and Ω represent the "accurate" wave functions, all of which are expressed in terms of orthonormal molecular orbitals ψ. Then we write the transformation expressing Ψ in terms of Ω's as a series of matrix transformations

$$\Psi = VDS^{-1}C\Omega \tag{1}$$

where C is the configuration interaction matrix (the identity, except for the Moskowitz set Ω_c); S^{-1} is the unitary matrix which is the inverse of the matrix generating spin eigenfunctions from single MO determinants; D is the matrix transforming single MO determinants into AO determinants; and V is the matrix transforming AO determinants into properly symmetrized VB spin eigenfunctions. Neither D nor V is unitary because of the nonorthogonality of VB functions. The construction of S^{-1} and V is straightforward. The matrix D is the inverse of a matrix whose construction was described by Moffitt.[10] The transformation from AO's π to MO's ψ is given in terms of a unitary matrix u and a diagonal matrix d (eq 2). We consider only the

$$\varphi = du\pi = \gamma\pi \tag{2}$$

case for which the z component of spin is zero, so that there are as many electrons with spin $+\hbar/2$ as with $-\hbar/2$. Then, the indices 1, 2, and 3 are reserved for spin orbitals with $\hbar/2$ z spin and indices 4, 5, and 6 for spin orbitals with $-\hbar/2$ spin. Then the matrix element of D connecting a determinant based on MO's α_1, ..., α_n with a determinant based on AO's β_1, ..., β_{2n}, can be written as shown in eq 3.

$$D^{\alpha_1\alpha_2\ldots\alpha_{2n}}_{\beta_1\beta_2\ldots\beta_{2n}} = \frac{\left(u^{\beta_1\ldots\beta_n}_{\alpha_1\ldots\alpha_n}\right)\left(u^{\beta_{n+1}\ldots\beta_{2n}}_{\alpha_{n+1}\ldots\alpha_{2n}}\right)}{d_{\alpha_1}\ldots d_{\alpha_{2n}}} \tag{3}$$

$$= \frac{\left|u^{\beta_1}_{\alpha_1}\ldots u^{\beta_n}_{\alpha_n}\right|\ \left|u^{\beta_{n+1}}_{\alpha_{n+1}}\ldots u^{\beta_{2n}}_{\alpha_{2n}}\right|}{d_{\alpha_1}\ldots d_{\alpha_{2n}}}$$

The symbol

$$u^{\beta_1\ldots\beta_n}_{\alpha_1\ldots\alpha_n}$$

(10) W. Moffitt, *Proc. Roy. Soc.* (London), **A218**, 486 (1953).

denotes the determinant formed from the minor of the u matrix from the elements indicated. The quantities d_{α_j} are the α_j-α_j elements of the diagonal matrix d.

The entire transformation was set up for machine computation. For a given state and molecular geometry, the choice of functions to use for the Ω set was reflected only in the set of atomic overlap integrals one put into the input deck. For reference, the overlaps are given in Table IV.

Appendix 2. Estimation of the Distorted Ground-State Wave Function

In the D_{3h} configuration of benzene, the optimum mixture between the e'' and e''_* orbitals is found by first orthogonalizing the pair of mixed orbitals and then minimizing the energy of the mixed pair. For example in the D_{3h} representation e'', the e_{1g} function, $\phi = C_1(\pi_1 + \pi_2 - \pi_4 - \pi_5)$, becomes nonorthogonal to the function $\phi_2 = C_2(\pi_1 + \pi_2 - 2\pi_3 + \pi_4 + \pi_5 - 2\pi_6)$; their overlap integral S_{12} is proportional to the difference between the overlap integrals $(\pi_1 \mid \pi_2)$ and $(\pi_2 \mid \pi_3)$. The secular equation was set up in terms of ϕ_1 and the function, $[\phi_2 - (\phi_1 \mid \phi_2)\phi_1]$, Schmidt-orthogonalized to ϕ_1. The elements of the secular determinant are

$$H_{11}$$

$$H_{12}' = H_{12} - S_{12}H_{11}$$

$$H_{22}' = H_{22} - 2S_{12}H_{12} + S_{12}{}^2H_{11}$$

where

$$H_{11} = d_1{}^2 u_{1i}u_{1j}h_{ij} \qquad h_{ij} = (\pi_i \mid \mathcal{K} \mid \pi_j)$$

$$H_{12} = d_1 d_2 u_{1i}u_{2j}h_{ij}$$

$$H_{22} = d_2{}^2 u_{2j}u_{2j}h_{ij}$$

using the Einstein summation convention. Elements h_{ij} were taken as $h_{ii} = 11.54$ ev = the valence-state ionization potential,[11] and h_{ij} as resonance integrals obtained by numerical integration of a Goeppert-Mayer-Sklar core potential for the different bond lengths involved.[12]

(11) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953); R. S. Mulliken, *ibid.*, **2**, 782 (1934).

(12) S. I. Choi, J. Jortner, S. A. Rice, and R. Silbey, *ibid.*, **41**, 3294 (1964).