Are There π Bonds in Benzene?

Peter A. Schultz
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

and

Richard P. Messmer
General Electric Corporate Research and Development, Schenectady, New York 12301, and
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 2 September 1986)

The wave function of benzene may be described in terms of two components corresponding to the Kekulé structures. Theoretical evidence is presented which indicates that the optimal orbitals comprising these structures form alternating single bonds and double *bent bonds* rather than the conventional σ and π bonds. *Ab initio* calculations which incorporate electronic correlation effects and explicitly treat resonance demonstrate that the bent-bond description is *energetically* the better representation of the ground state.

PACS numbers: 31.20.Tz

The nature of bonding in benzene, the prototypic aromatic molecule, has intrigued scientists for over one hundred years, ever since the tetravalent nature of the carbon atom was realized. However, the most enduring of the many models proposed for the structure and bonding of this molecule is that of Kekulé's "oscillating" structures.[1] With the advent of quantum mechanics and the subsequent development of valence-bond (VB) theory,[2–5] this description of the benzene molecule began to acquire a more concrete physical basis.[6] For benzene, a single bonding structure is not adequate to describe the system. At least two structures are required, symbolized by the Kekulé structures A and B of Fig. 1(a). The molecule is not described by one structure or the other, but partakes of some of the character of both. The anomalous stability of this molecule is commonly ascribed to the "resonance" of these two structures.

An exact N-electron wave function is rarely realizable, but an approximate wave function always may be written as a finite sum:

$$\Psi_{\text{approx}} = \sum\nolimits_I c_I \Psi_I \approx \Psi_{\text{exact}}, \tag{1}$$

where the Ψ_I may be, but need not necessarily be, simple determinants. It is desirable that Ψ_{approx} have a simple physical interpretation, and thus we might consider an approximate wave function for benzene as a superposition of two terms, each corresponding to one of the Kekulé structures.[6] What needs to be defined, then, is the nature of Ψ_A and Ψ_B used to describe the individual VB structures. In the generalized-VB (GVB) approach,[5] each Ψ_I is written as a product of N overlapping orbitals Ψ_i^I, each occupied by a single electron, with a general N-electron spin function Θ_N^I, i.e., Ψ_I has the form

$$\Psi_I^{\text{GVB}} = \mathcal{A}[\psi_1^I \psi_2^I \psi_3^I \cdots \Psi_N^I \Theta_N^I]. \tag{2}$$

This is the most general wave function that retains single-particle–single-orbital interpretability. As benzene is considered the canonical σ,π molecule, the usual description would be a ring with six C—C σ bonds and three C—C π bonds as schematically depicted in Fig. 1(b). In this Letter, we present new results using correlated *ab initio* wave functions, that can be interpreted within the context of Eqs. (1) and (2) and which suggest a new spatial description of the underlying VB structure, namely, the double bonds of benzene are best described, by use of the variational principle, in terms of Ω bonds[7]

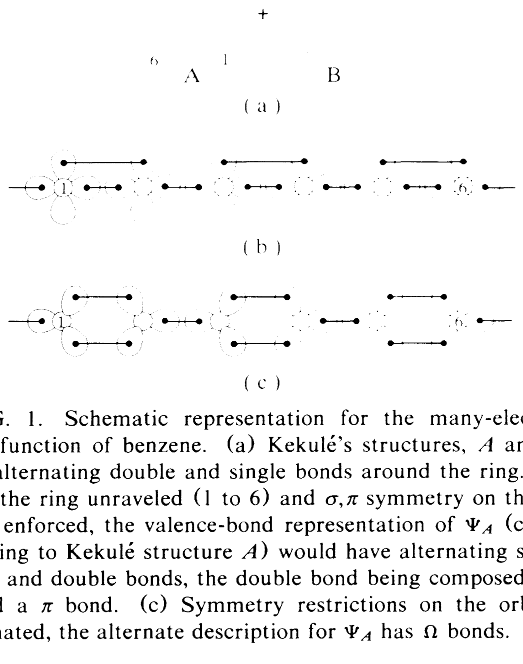


FIG. 1. Schematic representation for the many-electron wave function of benzene. (a) Kekulé's structures, A and B, with alternating double and single bonds around the ring. (b) With the ring unraveled (1 to 6) and σ,π symmetry on the orbitals enforced, the valence-bond representation of Ψ_A (corresponding to Kekulé structure A) would have alternating single bonds and double bonds, the double bond being composed of a σ and a π bond. (c) Symmetry restrictions on the orbitals eliminated, the alternate description for Ψ_A has Ω bonds.

(equivalent bent bonds[8]), schematically depicted in Fig. 1(c), instead of the usually assumed σ and π bonds.

The notion of equivalent double bonds has had an intuitive and aesthetic appeal for a long time, and within molecular-orbital (MO) theory there has been much speculation about the merit of localized orbitals and equivalent orbitals for multiple bonds,[9] once directed even toward benzene.[10] A unique interpretation of the bonding, however, is not possible within MO theory because of an ambiguity inherent to any mean-field approach: The energy is invariant to any unitary transformation of the occupied orbitals. The canonical orbitals of MO theory have σ and π symmetry, and therefore it has become commonplace to divide the problem into σ and π subspaces,[11-14] although the more sophisticated *ab initio* investigations have questioned the validity of this separation.[12-14] With correlation effects explicitly included in the wave function, the above invariance to a unitary transformation no longer holds, and the merit of different qualitative descriptions potentially can be assessed quantitatively. Conventional configuration-interaction (CI) calculations [expansions of Eq. (1) in simple orthogonal determinants] generally lack such simple interpretability, however, and a complete CI, like the mean-field result, cannot distinguish between the two bonding descriptions. Thus, the approach used here, while not the most general possible, incorporates a substantial amount of correlation in the wave function and retains a simple bonding interpretation which allows an energetic evaluation of the better bonding configuration.

The computational method we employ is the perfect-pairing (PP) approximation of the GVB approach.[5] The valence electrons of Ψ_I^{PP} are described as generalized Heitler-London pairs:

$$\Phi_i = \psi_{i,1}\psi_{i,2}(\alpha\beta - \beta\alpha), \tag{3}$$

where the forms of the singlet-coupled, overlapping spatial orbitals $\psi_{i,1}, \psi_{i,2}$ are variationally determined, subject to the restriction that orbitals of different pairs be orthogonal. Ψ_I^{PP} is the antisymmetrized product of these pair functions:

$$\Psi_I^{\mathrm{PP}} = \mathcal{A}[\Phi_1^I \Phi_2^I \cdots \Phi_N^I], \tag{4}$$

which is clearly of the form of Eq. (2) and thus Ψ_I^{PP} approximates Ψ_I^{GVB} of Eq. (2). If the pairs of electrons are restricted to occupy the same orbital so that $\psi_{i,1} = \psi_{i,2}$, Eq. (3) reduces to the Hartree-Fock (HF) form. For benzene, the singly occupied orbitals of Ψ_A (dropping the assumed PP label) will resemble those of the schematic diagrams of Fig. 1(b) or 1(c), depending on whether the orbitals of the double bonds are restricted to have σ,π symmetry or not. We approximate the exact wave function using two terms[15]:

$$\Psi_{\mathrm{tot}} = c(\Psi_A + \Psi_B), \tag{5}$$

with the calculation carried out using the resonating-PP (RPP) method.[16,17] In this method, the orbitals of the individual structures, Ψ_A and Ψ_B, are not allowed to reoptimize in the presence of the resonance. The method is analogous to a CI calculation except that Ψ_A and Ψ_B are each multideterminant functions and are *nonorthogonal.* The extra energy stabilization given by Ψ_{tot} with respect to the individual energies of Ψ_A and Ψ_B is termed the resonance energy, i.e.,

$$E_{\mathrm{res}} = E_{I,I} - E_{\mathrm{tot}}, \tag{6a}$$

$$E_{I,I} = \langle \Psi_I | H | \Psi_I \rangle, \quad I = A, B, \tag{6b}$$

and we note that $E_{A,A} = E_{B,B}$.

The calculations for benzene were performed at the experimental geometry[18] (D_{6h}, $R_{\mathrm{C\text{-}C}} = 1.397$ Å, $R_{\mathrm{C\text{-}H}} = 1.084$ Å). Standard valence double-zeta basis sets were used for all atoms.[19] A summary of the energies for the various approximate wave functions from HF, GVB-PP[20] (and PPCI[21]), and RPP[22] calculations is given in Table I. The designation of the approximate wave functions and the extent of electronic correlation included are as follows: (a) HF: no electrons are correlated; (b) PP(3): the three C—C π bonds; (c) PP(9): the nine C—C bonds of the carbon ring. The σ,π-bonded and Ω-bonded PP descriptions of Ψ_A are nearly equivalent in energy. This equivalence may be more apparent than real. Restrictions in the PP description with respect to the full GVB result (particularly maintaining orthogonality between orbitals of different pairs) bias it against the Ω-bonded description *vis-à-vis* the σ,π description.[23] For example, the σ,π description of the ethylene double bond is favored by use of PP[24]; relieving the orthogonality restrictions results in bent bonds,[25] while relieving the PP spin restrictions within the double bond is not energetically important.[26] Thus, with three double bonds, evidence suggests that benzene should prefer Ω bonds even before one considers the mixing of the two Kekulé terms. At the HF level, of course, the two descriptions are identical because of the already noted invariance in the wave function.

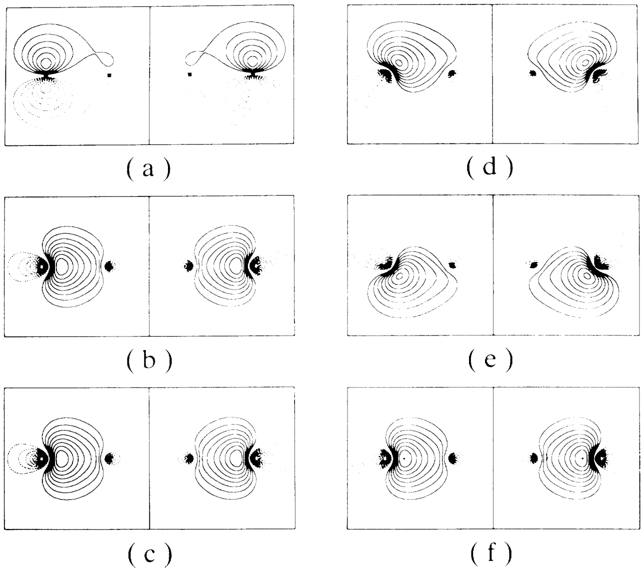
Focusing the discussion initially on the PP description obtained by restriction of the orbitals to be of σ and π symmetries, the energetically most important electron

TABLE I. Total energies for σ,π- and Ω-bonded calculations for benzene. All energies are in hartrees.

Calculation	σ,π bond result	Ω bond result
HF	−230.64037	−230.64037
PP(3)	−230.68507	a
RPP	−230.69691	a
PP(9)	−230.75047	−230.74837
PPCI(130)	−230.75047	−230.74837
RPPCI	−230.76236	−230.77755

[a] The PP(3 pairs) calculation for the Ω-bonded structure is undefined.

pairs to correlate are those arising from the six π electrons. The PP(3) description of Ψ_A gains 0.41 eV/pair over the HF description. Correlating the six C—C σ bonds in the PP(9) result gains an additional 0.30 eV/pair for each C—C σ bond. Examining the contour plots in Figs. 2(a)–2(c) for the orbitals of the PP(9) result reveals a close correspondence with the schematic diagram of Fig. 1(b). The contour plots shown in Fig. 2(a) of the two orbitals comprising a π pair reveal that the orbitals, each occupied by a single electron, are quite localized, forming a π bond between neighboring sites, while the σ orbitals, shown in the contour plots of Figs. 2(b) and 2(c), clearly represent normal C—C σ bonds. The resonance energy, E_{res}, obtained by taking the superposition of the PP results $\Psi_A^{\sigma\pi}$ and $\Psi_B^{\sigma\pi}$ in the RPP total wave function [Eqs. (5) and (6)] is 0.32 eV, regardless of whether the C-C σ pairs are correlated. This value represents but 20% of the experimental net resonance stabilization of 1.6 eV.[4] A self-consistent RPP(3) calculation for benzene[17] (the orbitals are allowed to relax in the presence of resonance) yields an improved resonance energy of 0.59 eV, a value which also should not change when the C-C σ pairs are correlated. Hence, the calculated resonance stabilization for a system divided into σ and π orbitals falls far short of the value which is the key empirical observation about the stability of this molecule.


(a) (d)

(b) (e)

(c) (f)

FIG. 2. Orbital-amplitude contour plots from PP calculations for benzene, in a plane perpendicular to the molecular plane along a C-C internuclear axis. Contours start at ± 0.10 a.u. and proceed in 0.05-a.u. increments. Solid lines denote positive contours, dashed lines negative contours. Panels (a)–(c) are from $\Psi_A^{\sigma\pi}$. (a) The two orbitals comprising a π pair. One orbital, occupied by a single electron, is localized on the left carbon atom while the other is localized on the right, forming a bond. (b) The C—C σ bond of the double bond. (c) The orbitals forming a neighboring C—C single σ bond. Panels (d)–(f) are from Ψ_A^{Ω}. (d),(e) The two pairs forming the Ω bonds between the two carbon atoms. (f) The orbitals forming a neighboring C—C single bond.

When symmetry restrictions on the orbitals are removed, a qualitative change occurs in the description of the wave function. For the PP(9) result, the orbitals of Figs. 2(d)–2(f) are obtained. Noting the schematic description of Fig. 1(c), we observe that the orbitals have adopted a form that corresponds to Ω bonds [Figs. 2(d) and 2(e)] and single σ bonds [Fig. 2(f)], alternating around the ring. In contrast to the sp^2-hybridized carbon atoms of the symmetry-restricted calculation, each carbon atom is approximately tetrahedrally coordinated, with two of the hybrids on one center directed toward a single neighboring carbon atom which, in turn, has two hybrids directed toward the first atom in order to form Ω bonds.

While the PP(9) energy of Ψ_A^{Ω} approximately equals that of $\Psi_A^{\sigma\pi}$, the resonance energy for the former is dramatically larger, i.e., 0.79 eV, or 0.47 eV better than for the analogous σ,π calculation. This value is even larger than the 0.59-eV self-consistent resonance energy obtained for the π-electron [PP(3)] system.[17,27] Hence, Ω-bonded benzene appears to be a good representation of the individual Kekulé VB structures and, in any case, is a better representation of the ground state than σ,π-bonded benzene, i.e., $\Psi_{\text{tot}}^{\Omega}$ is 0.41 eV lower in energy than $\Psi_{\text{tot}}^{\sigma\pi}$.

We believe that the VB method has a significant advantage over MO theory or potentially more precise CI calculations in that it retains an interpretability that bears a direct relationship to the almost universally accepted concepts of structural chemistry while incorporating important correlation effects. The valence-bond approach provides a rationalization for why bond properties, such as energy, bond length, force constant, should be transferable between different molecules,[4] and even between molecules and solids.[28] Here, however, the transferability has been shown to penetrate one level deeper: The atomic contributions to those bonds are determined by the characteristic hybrids of the bonding atoms, in this case tetrahedral carbon atoms. Approximate tetrahedral coordination for carbon has been exhibited recently for carbon atoms involved in double bonds (in CO_2)[7] and in triple bonds (difluoroacetylene).[23] Here we have demonstrated that this behavior extends to what usually has been considered a π-electron system of sp^2-hybridized carbon atoms.

This work was supported in part by the National Science Foundation Materials Research Laboratory Program under Grant No. DMR-8519059 at the Laboratory for Research on the Structure of Matter, University of Pennsylvania. We would like to express our gratitude for the assistance rendered by Dr. S. H. Lamson of General Electric in the Cray computations used in this work.

[1] A. Kekulé, Justus Liebigs Ann. Chem. **162**, 77 (1872).

[2] W. Heitler and F. London, Z. Phys. **44**, 455 (1927).

[3] A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. London, Ser. A **220**, 446 (1953).

[4] L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, NY, 1960), 3rd ed.

[5] W. J. Hunt, P. J. Hay, and W. A. Goddard, III, J. Chem. Phys. **57**, 738 (1972); W. A. Goddard, III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Acc. Chem. Res. **6**, 368 (1973); F. W. Bobrowicz and W. A. Goddard, III, in *Methods of Electronic Structure Theory, Modern Theoretical Chemistry Vol. 3,* edited by H. F. Schaefer, III (Plenum, New York, 1977), p. 79.

[6] J. C. Slater, Phys. Rev. **37**, 481 (1931).

[7] R. P. Messmer, P. A. Schultz, R. C. Tatar, and H.-J. Freund, Chem. Phys. Lett. **126**, 176 (1986).

[8] Ω bonds refers to equivalent bent bonds in multiply bonded systems as opposed to the bent single result from geometry considerations in such strained molecules as the propellanes.

[9] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. London, Ser. A **202**, 166 (1950); J. M. Foster and S. F. Boys, Rev. Mod. Phys. **35**, 300 (1960); C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963).

[10] M. D. Newton and E. Switkes, J. Chem. Phys. **54**, 3179 (1971).

[11] J. M. Norbeck and G. A. Gallup, J. Am. Chem. Soc. **95**, 4460 (1973), and **96**, 3386 (1974).

[12] T. H. Dunning, Jr., W. J. Hunt, and W. A. Goddard, III, Chem. Phys. Lett. **4**, 147 (1969).

[13] C. F. Bender, T. H. Dunning, Jr., H. F. Schaefer, III, W. A. Goddard, III, and W. J. Hunt, Chem. Phys. Lett. **15**, 171 (1972).

[14] P. J. Hay and I. Shavitt, Chem. Phys. Lett. **22**, 33 (1972), and J. Chem. Phys. **60**, 2865 (1974).

[15] The terms associated with the Kekulé structures prove dominant. Terms associated with Dewar structures are of little energetic consequence (<0.05 eV net stabilization) when included in the calculation. Ionic terms found important in a VB calculation (Ref. 11) are included self-consistently in $\Psi^{\rm PP}$.

[16] A. F. Voter and W. A. Goddard, III, Chem. Phys. **57**, 253 (1982).

[17] A. F. Voter, Ph.D. thesis, California Institute of Technology, 1983 (unpublished).

[18] G. Herzberg, in *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, NJ, 1966), p. 666.

[19] T. H. Dunning, Jr. and P. J. Hay, in *Methods of Electronic Structure Theory,* Modern Theoretical Chemistry Vol. 3, edited by H. F. Schaefer, III (Plenum, New York, 1977), p. 1. Polarization functions are not expected to affect the relative energetics and are omitted. The addition of carbon d functions in C_2H_4 calculations benefits the Ω description 0.06 eV more than the σ,π description.

[20] R. A. Bair, W. A. Goddard, III, A. F. Voter, A. K. Rappé, L. G. Yaffe, F. W. Bobrowicz, W. R. Wadt, P. J. Hay, and W. J. Hunt, GVB2P5 Program (unpublished); see R. A. Bair, Ph.D. thesis, California Institute of Technology, 1980 (unpublished); see also Ref. 5.

[21] $\Psi^{\rm PP}$ can also be written as a conventional CI expansion of 2^N terms, N being the number of correlated pairs. RPP calculations with a large number of correlated pairs proved computationally impractical and a truncated configuration list of the leading M terms of the CI expansion was used to give a good approximation (within 0.000002 hartree) to $\Psi^{\rm PP}$. These results are denoted PPCI(M) and RPPCI.

[22] Program RGVB written by C. M. Kao and P. A. Schultz based on the method of Ref. 16.

[23] R. P. Messmer and P. A. Schultz, Phys. Rev. Lett. **57**, 2653 (1986).

[24] P. J. Hay, W. J. Hunt, and W. A. Goddard, III, J. Am. Chem. Soc. **94**, 8293 (1972).

[25] W. E. Palke, J. Am. Chem. Soc. **108**, 6543 (1986).

[26] P. A. Schultz and R. P. Messmer, unpublished.

[27] A self-consistent resonance calculation for Ω-bonded benzene will clearly increase $E^{\Omega}_{\rm res}$.

[28] P. A. Schultz and R. P. Messmer, Phys. Rev. B **34**, 2532 (1986).