Valence-Bond Calculation of the Electronic Structure of Benzene

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Abstract: Nonempirical, *ab initio* calculations of the electronic structure of the ground state of benzene have been made. The AO basis used is the same as that of a "full π" MO–CI calculation already in the literature, and the 22 $^1A_{1g}$ states obtained in this treatment are identical with those obtained before. The lowest energy is -230.4546 au with equilibrium separations of the nuclei. The VB results obtained here differ strongly from those of the corresponding semiempirical treatments that have been done heretofore, in that the wave function contains a far larger contribution from basis functions of the polar type. The nature of the differences between the two methods is investigated by calculating a number of properties of the wave function. Among those determined are the first-order, spinless density matrices corresponding to the various bonding schemes, and it is found that the symmetry VB function representing the singly ortho polar structures has a very large bond order between ortho positions and that this explains the surprisingly high stability of this function. The resonance energy of benzene is also considered, and it is found that the traditional procedure yields poor results. However, when a more sophisticated form of the wave functions for the localized and delocalized structures is used, a value of 61.4 kcal is obtained for the vertical resonance energy. This compares very well with the value of 66.0 kcal obtained from experimental data.

Benzene is the archetypal aromatic hydrocarbon, and over the years it has been used as a test of many chemical theories, both qualitative and quantitive. Thus, among the early tests of quantum mechanics on molecular systems, the one on benzene done by Pauling and Wheland[2] occupies a position important both intrinsically and because it provided a qualitative picture capable of extension to more complicated aromatic hydrocarbons. These workers used Slater's[3a] generalization of the Heitler–London H_2 wave function,[3b] and applied this to the π electrons only. In a remarkable synthesis of the ideas of classical bonding theory and the graphical method of determining linearly independent valence-bond wave functions discovered by Rumer,[4] Pauling and Wheland were able to show that benzene could be considered a superposition of the various Kekule and Dewar bonding schemes proposed much earlier. The analysis was highly approximate of course, with many estimates and assumptions concerning the unimportance of supposedly small quantities, since at the time these calculations were done there was no possibility of an *ab initio* study of a system this large. The years immediately following produced no satisfactory quantitative methods for handling VB wave functions, and in 1950 it was still necessary for Craig[5] to use most of the same approximations in a discussion of benzene which included polar type resonance structures in the wave function. In this study he found the polar functions to comprise only a small fraction of the total wave function, and this type of structure has since been considered unimportant in benzene.

Since 1950 the development of methods to handle VB calculations in a more quantitative fashion has been slow. However, the formulas of Lowdin[6] for matrix elements of determinal wave functions with nonorthog-

onal orbitals have provided one of the links in a practical method for *ab initio* VB calculations. The other part of the process requires the expression of the VB functions in Slater determinants,[7] and with the present capability of computers several calculations have been done in the last few years.[8] In this connection a question of nomenclature has also arisen. Several "valence-bond" methods have been suggested recently[9] which use various amounts of orthogonalization to simplify the calculations. Therefore, this term has different meanings for different workers, and for purposes of definiteness we state that the expression "valence bond" is reserved to have its traditional sense for this article. Thus we use nonorthogonalized AO's of the appropriate atoms just as they stand. Actually, we modify this position somewhat, also, as will be described later.

In this laboratory a still different method for dealing with VB wave functions has been developed. The procedure involves expressing the VB function in terms of the Young operator, θNPN,[10] and among the presently available methods this one appears to be the most economical of computer effort.

During the time that the approximate VB calculations were being done there was no indication either from the theory itself or the comparisons with experiment that these results were grossly incorrect, and it was felt that the various approximations used made only relatively small quantitative distortions of the results. Nevertheless, now that methods for doing VB calculations have been developed to the point where *ab initio* treatments are possible, it is important to test this supposition. Using benzene as a test molecule we have performed VB calculations to investigate this question. A preliminary report of the results has been given already,[11] and the present article is a more complete

(1) NDEA Predoctoral Fellow, 1972–1973.
(2) L. Pauling and G. Wheland, *J. Chem. Phys.*, 1, 362 (1933).
(3) (a) J. C. Slater, *Phys. Rev.*, 37, 481 (1931); 38, 1109 (1931); (b) W. Heitler and F. London, *Z. Phys.*, 44, 455 (1927).
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(5) D. P. Craig, *Proc. Roy. Soc., Ser. A*, 200, 401 (1950).
(6) P.-O. Lowdin, *Phys. Rev.*, 97, 1474 (1955).

(7) J. C. Slater, *J. Chem. Phys.*, 19, 220 (1951).
(8) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, 91, 807 (1969).
(9) R. McWeeny, *Proc. Roy. Soc., Ser. A*, 223, 63, 306 (1954); 227, 288 (1955); W. J. Hunt, P. J. Hay, and W. A. Goddard, *J. Chem. Phys.*, 57, 738 (1972).
(10) G. A. Gallup, *Int. J. Quantum Chem.*, 6, 761, 899 (1972).
(11) J. M. Norbeck and G. A. Gallup, *J. Amer. Chem. Soc.*, 95, 4460 (1973).

report. As was seen in the earlier communication the *ab initio* calculation has aspects in striking disagreement with the previous approximate treatments. This fact immediately raises two questions: (1) what is it about the standard approximations used in earlier work that has caused the results to differ so far from the *ab initio*, and (2) what consequences, if any, do the new results have for the way that chemists should look upon the electronic structure of benzene and other aromatic hydrocarbons?

The first of these questions is far easier to answer than is the second, and its discussion constitutes the major portion of this article. We shall return to the other question more briefly in the Conclusion.

Detailed Description of Calculation

The previous, approximate calculations of the structure of the benzene molecule have all been done with the neglect of the 36 electrons comprising the σ bonds and the 1s shells of the carbon atoms, and the actual calculations involved just the six π electrons. The effects of the core were estimated and included in terms of certain "penetration" integrals, the values of which do not effect differences in energy. Such a treatment of the σ electrons is not suitable for an *ab initio* calculation, of course, and it is necessary for us to use a different approach to handle these electrons. Among the various possibilities that might be tried, we have chosen to use the 18 σ-type molecular orbitals from the SCF calculation as the functions for the electrons in question, and the six p_z orbitals at the carbons are used for the remaining electrons, of course. There are two reasons that this choice is made. 1. It is felt that the properties of the π electrons will be reasonably insensitive to the detailed form of the functions representing the σ electrons, and these molecular orbitals are the simplest accurate form for them. 2. The set of functions constructed in the way we have described spans the same linear space as the set of functions obtained by opening only the π molecular orbitals and doing a "full" CI after an SCF calculation. Thus if the same AO basis were used, the present VB calculation and the "full" π MO–CI should give identical results. Actually, we have used exactly the same AO basis as that used by Buenker, Whitten, and Petke,[12] and the VB and the MO–CI results are identical.

If all the possible bonding schemes are drawn for the six p_z orbitals one obtains 22 different types, and these are shown in Figure 1. The Rumer diagrams for the construction of the VB functions can follow these bonding diagrams exactly, since we are working with singlet states. Each of these bonding schemes gives rise to a linearly independent symmetry function, and the arabic numeral given in the figure shows the number of VB functions in the corresponding symmetry function. The results of ref 10 are directly usable here, and, for example, the function corresponding to I is

$$\Psi_{\mathrm{I}} = \theta\mathrm{NPN}\{4p_1(1)p_2(4)p_3(2)p_4(5)p_5(3)p_6(6) -$$
$$2p_1(1)p_2(4)p_3(2)p_4(3)p_5(5)p_6(6) -$$
$$2p_1(1)p_2(2)p_3(4)p_4(5)p_5(3)p_6(6) +$$
$$p_1(1)p_2(2)p_3(4)p_4(3)p_5(5)p_6(6) -$$
$$3p_1(1)p_2(2)p_3(3)p_4(4)p_5(5)p_6(6)\}\ \Xi(7, \ldots, 42) \quad (1)$$

(12) R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2261 (1968).
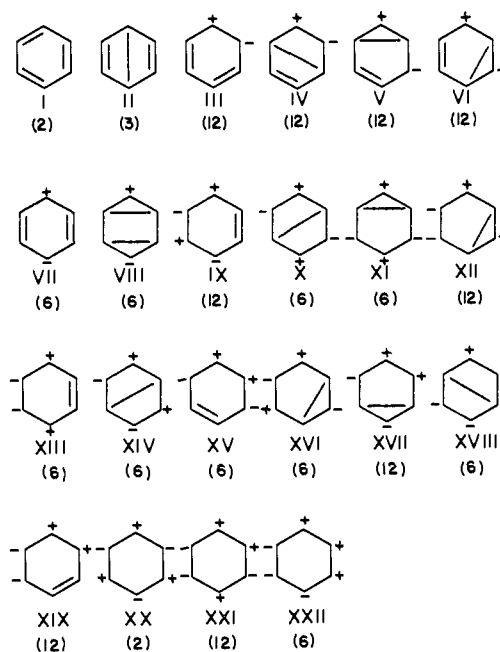

Figure 1. Representative rumer diagrams and number of equivalent structures for each of the 22 $^1A_{1g}$ symmetry functions.

where Ξ represents a product function of the σ orbitals with the numbering arranged to match the numbering in θNPN correctly. This function as it is written is also not yet normalized.

Actually the generation of these different VB functions and the projection of the corresponding spatial symmetry functions is fully automated in the programs used to make these calculations. The use of exactly projected symmetry functions reduces significantly the labor of constructing the matrix elements, since the turnover rule removes one operator in the expressions.

Throughout this article we will have occasion to represent both the individual VB function and the corresponding $^1A_{1g}$ symmetry function by the Roman numerals given in Figure 1. To avoid confusion we indicate the symmetry function by an asterisk. Thus, VI is used to represent the individual VB function with π bonds between carbons 2–4 and 5–6. This function also has carbon 3 negatively charged. On the other hand, the symbol VI* is used to represent the $^1A_{1g}$ symmetry function corresponding to this same bonding diagram. There are 12 terms in this function.

After the matrices for H and S are generated the eigenvalues and the eigenvectors are obtained by standard techniques. The occupation numbers are determined by an inverse-overlap population analysis.[13] Such occupation numbers take into consideration the unique aspect of each function and compensate for their mutual overlaps.

The functions may for convenience be arranged in four groups according to the amount of polarity. Thus there are among the $^1A_{1g}$ symmetry functions 2 covalent, 6 singly polar, 11 doubly polar, and 3 triply polar types. These are constructed from the total of 175 individual bonding or Rumer diagrams. The results of several calculations are given in Table I. For comparison purposes the SCF energy was recalculated and this

(13) J. M. Norbeck and G. A. Gallup, *Chem. Phys. Lett.*, **21**, 495 (1973).

Table I. Comparison of Energies for Various Partial Calculations, the SCF, and the "Full" Calculation

	No. of symmetry functions	Energy, hartrees
Kekule	1	-230.2972
Kekule and Dewar	2	-230.3026
SCF	1	-230.3754
Ortho polar only	2	-230.3781
Covalent & ortho polar	4	-230.4125
Covalent & singly polar	8	-230.4373
"Full"	22	-230.4546

Table II. Diagonal Energies for 22 $^1A_{1g}$ Symmetry Functions[a]

Function	Diagonal energy	Covalent Eigenvector	Occ no.	Covalent and singly polar Eigenvector	Occ no.	"Full" Eigenvector	Occ no.
I*	-230.2972 (2)	0.6586	0.7760	0.2428	0.0622	0.2684	0.2192 (2)
II*	-230.2838 (3)	0.3539	0.2240	0.1335	0.0194	0.1353	0.0607 (6)
III*	-230.3244 (1)			0.3847	0.4753	0.2666	0.2528 (1)
IV*	-230.1732 (4)			0.2154	0.2756	0.1418	0.1447 (3)
V*	-230.0452 (6)			0.1383	0.0980	0.1156	0.0965 (4)
VI*	-229.7039 (11)			0.0282	0.0078	0.0281	0.0164 (12)
VII*	-229.8100 (7)			0.0600	0.0234	0.0483	0.0345 (7)
VIII*	-229.7185 (9)			0.0623	0.0381	0.0359	0.0241 (8)
IX*	-230.1039 (5)					0.1303	0.0622 (5)
X*	-229.7620 (8)					0.0425	0.0226 (9)
XI*	-229.7072 (10)					0.0386	0.0214 (10)
XII*	-229.3489 (18)					0.0090	0.0014 (17)
XIII*	-229.5664 (15)					0.0205	0.0061 (14)
XIV	-229.5412 (16)					0.0172	0.0053 (15)
XV*	-229.5810 (14)					0.0131	0.0025 (16)
XVI*	-229.7029 (12)					0.0359	0.0185 (11)
XVII*	-229.3398 (19)					0.0052	0.0005 (18)
XVIII*	-228.8900 (21)					0.0017	0.0001 (20)
XIX*	-229.2774 (20)					0.0010	0.0000 (21)
XX*	-229.6765 (13)					0.0283	0.0103 (13)
XXI*	-229.3699 (17)					0.0042	0.0002 (19)
XXII*	-228.4681 (22)					0.0003	0.0000 (22)
Energy		-230.3026		-230.4373		-230.4546	

[a] Eigenvectors and occupation numbers for various calculations discussed in the text.

value is also given in the table. The partial calculations done are Kekule only, covalent only (Pauling and Wheland's case), orthopolar only, covalent and orthopolar (Craig's case), covalent and singly polar, and finally, of course, the "full" π calculation. The diagonal energies of each of the symmetry functions and the coefficients and occupation numbers for three of the calculations are given in Table II. It will be noticed that the row labels in this table are asterisked and we emphasize that this means the entries refer to normalized symmetry functions and not to normalized functions corresponding to individual Rumer diagrams. The phases of the functions are arranged so that the coefficients are all positive, also.

Comparison with Previous Work

As was indicated in the introduction to this article the previous VB work on benzene is semiempirical in nature, and the early work by Pauling and Wheland gave the result that I* is approximately four times more important than II* in the wave function containing only covalent terms. In Table II the columns headed "Covalent" show the corresponding results for this *ab initio* calculation. Except for a very slight increase in the importance of the II* function, these results agree very well with the earlier semiempirical results.

Thus, at first glance, it appears that the approximations made by the early investigators were not too severe. However, the energy found here is seen to be 0.0728 au (45.7 kcal) above the SCF energy shown in Table I. This disagrees with the results obtained by Coulson and Newton[14] who compared the SCF and VB energies using the π electron model of Goeppert-Mayer and Sklar.[15] Their results, which were done with the neglect of nonnearest neighbor overlap and exchange integrals, show the SCF energy to be 6.7 kcal higher than the covalent only VB calculation. Recently further comparisons of the VB and SCF-MO-CO approaches have been published by Campion and Karplus.[16] They too used the Goeppert-Mayer and Sklar approximation and in the systems studied (allyl radical, *trans*-butadiene, and methylene cyclobutadienyl radical) found the covalent structures to give a lower energy than the corresponding SCF function. However, the *ab initio* results reported here and earlier[17] have always indicated that the SCF energy is lower than that obtained by using only covalent functions. The exact nature of the inadequacies of this approximate approach is not clear at the present.

An even more startling discrepancy between semiempirical and *ab initio* results is observed when the two ortho singly polar functions (III*, IV*) are included with the covalent pair. Table III shows the eigenvectors and the occupation numbers[13] for each case, and it is seen that there is practically a complete reversal of the importance of the covalent as compared to the polar functions. In fact, this result would be predicted from a careful examination of Table I, since there it is seen that the energy of the ortho polar alone function

(14) C. A. Coulson and M. D. Newton, *Mol. Phys.*, **15**, 305 (1968).
(15) M. Goeppert-Mayer and A. Sklar, *J. Chem. Phys.*, **6**, 219 (1938).
(16) W. J. Campion and M. Karplus, *Mol. Phys.*, **25**, 921 (1973).
(17) J. M. Norbeck and G. A. Gallup, *Int. J. Quantum Chem., Symp.*, **7**, 161 (1973).

Table III. Comparison of Semiempirical and *ab Initio* Calculation Including Covalent and Ortho Polar Symmetry Function

	Semiempirical[a]		Ab initio	
	Eigenvector	Occ no.	Eigenvector	Occ no.
I*	0.6179	0.4932	0.2487	0.0440
II*	0.3553	0.1631	0.1314	0.0127
III*	0.2385	0.2755	0.4832	0.6772
IV*	0.1187	0.0682	0.2534	0.2661

[a] See ref 5.

The entries are the squares of the expansion coefficients, which form a satisfactory set of occupation numbers, because the MO–CI basis is orthonormal. There is a slight complication with some of the configurations, *e.g.*, $a_{2u}e_{1g}{}^3e_{2u}b_{1g}$ is a case in point, since these give rise to two $^1A_{1g}$ functions, and the corresponding entry in Table IV is the sum of the squares from all of the functions of the configuration in such cases. It is easily seen that the ortho singly polar function has the smallest

Table IV. Expansion of VB Functions in Terms of MO–CI Functions

MO configuration											
a_{2u}	e_{1g}	e_{2u}	b_{1g}	I*	II*	III*	IV*	V*	VI*	VII*	VIII*
2	4	0	0	0.3882	0.2900	0.7569	0.6083	0.4652	0.4728	0.3527	0.2305
2	2	2	0	0.3456	0.2811	0.1717	0.2062	0.2029	0.2062	0.3140	0.2091
2	2	0	2	0.0099	0.0	0.0094	0.0	0.1449	0.0	0.0090	0.0459
1	3	1	1	0.1196	0.1137	0.0142	0.0361	0.0355	0.0361	0.1142	0.0788
0	4	2	0	0.0095	0.0	0.0090	0.1413	0.0	0.1413	0.0086	0.0441
0	4	0	2	0.0057	0.0231	0.0	0.0	0.0	0.0	0.0467	0.0598
2	1	2	1	0.0145	0.0	0.0035	0.0543	0.0	0.0543	0.0132	0.0677
1	2	3	1	0.0142	0.0	0.0034	0.0	0.0523	0.0	0.0134	0.0665
1	2	1	2	0.0076	0.0	0.0018	0.0285	0.0	0.0285	0.0069	0.0355
0	3	2	1	0.0075	0.0	0.0018	0.0	0.0274	0.0	0.0069	0.0349
2	0	4	0	0.0060	0.0245	0.0	0.0	0.0	0.0	0.0493	0.0631
2	0	2	2	0.0029	0.0	0.0027	0.0	0.0421	0.0	0.0026	0.0134
1	1	3	1	0.0365	0.0343	0.0047	0.0105	0.0103	0.0105	0.0332	0.0229
0	2	4	0	0.0021	0.0	0.0020	0.0308	0.0	0.0308	0.0019	0.0096
0	2	2	2	0.0277	0.0225	0.0137	0.0165	0.0162	0.0165	0.0251	0.0167
0	0	4	2	0.0026	0.0020	0.0051	0.0032	0.0031	0.0032	0.0024	0.0016

is 0.076 au (47.7 kcal) lower than the covalent only function. It is further seen that the best convergence rate to the "full" value is not obtained by introducing new functions in the same order as would be suggested by the semiempirical results.

We also point out the somewhat unexpected fact that the diagonal energy of III* is 0.027 au (16.9 kcal) lower than the corresponding value for I* as can be seen from Table II. This is also in direct contradiction to the semiempirical results.

From the foregoing comparisons it is seen that there are serious differences between the results of the two approaches, and it is certainly not obvious from an examination of only the energies and the wave functions given so far where the difficulties lie. The various VB wave functions are multielectron functions and as such resist a simple interpretation and understanding. It was thought that these functions were understood, of course, but the results described above cast considerable doubt on this. In order to attempt a better understanding of the properties of VB wave functions, we have made several analyses of these functions into other terms and in particular into simpler forms. This has been done for the covalent and singly polar functions only, since this subset adequately displays the discrepancies between the *ab initio* and semiempirical approaches.

Expansion of VB Functions in Terms of MO–CI Functions

The set of VB functions and the set of MO–CI functions span the same linear space, and therefore, either set serves as a basis for this space. In particular, therefore, the VB functions may be expressed as linear combinations of the MO–CI functions. These calculations have been made, and the results are shown in Table IV.

contributions from the excited states, and this certainly confirms the importance of this term in the total wave function. It may be pointed out that the square roots of the entries in Table IV in those cases where there is only one function per configuration is just the magnitude of the overlap, and hence, we see that the overlap between the SCF function and III* is 0.870, which shows that there is considerable similarity between these two functions. It is also observed that the configurations giving rise to $^1A_{1g}$ functions involve double, triple, quadruple, and sextuple excitations. Thus none of the $^1A_{1g}$ VB symmetry functions include singly excited MO configurations, which are well known to be present in ground state CI wave functions to only a minor extent.

Spinless, First-Order Density Matrices for VB Functions

The expansions discussed in the last section represent one type of multielectron wave function in terms of another type. This does not provide any real simplification for the understanding of the properties of these functions. In this section we give the first-order density matrices for each of the basis function, I* through VIII*. These densities provide a single-particle picture of the VB functions for determining a qualitative picture of their properties. Because of the orthogonality between the σ and the π electron orbitals in this system, this density is separable into two parts corresponding to these types of orbitals. Thus we have

$$\gamma(1|1') = 42\int \psi(1', 2, \ldots, 42)^*\psi(1, 2, \ldots, 42) \times$$
$$d\tau_1 = \gamma_\sigma(1|1') + \sum_{i,j}\gamma_{ij}p_i(1)p_j(1') \quad (2)$$

where the portion corresponding to the σ elections has

Table V. Values of q_i and q_{ij} for VB Symmetry Functions

Function	q_1	q_{12}	q_{13}	q_{14}
I*	0.9422	0.0742	−0.0144	−0.0021
II*	0.9504	0.0658	−0.0146	−0.0016
III*	0.8143	0.2118	−0.0160	−0.0100
IV*	0.8605	0.1622	−0.0162	−0.0064
V*	0.9419	0.0622	0.0048	−0.0090
VI*	0.9224	0.1048	−0.0230	−0.0041
VII*	0.9658	0.0490	−0.0132	−0.0015
VIII*	1.0459	−0.0386	−0.0062	−0.0010
Covalent only	0.9391	0.0778	−0.0149	−0.0020
Covalent and singly polar	0.7973	0.2302	−0.0151	−0.0124

atoms, while the Kekule function, I*, has a relatively small bond order between these positions. The bonding between centers mutually meta and para is slightly antibonding in all cases except for the function V*, which is slightly bonding for meta pairs. Examination of the bonding diagram for V* shows that this is certainly consistent. However, among all of the entries in the table, the wave function consisting of the covalent and the singly polar functions has the greatest bonding between ortho positions.

The charge and bond orders given in Table V are for the symmetry functions based upon the particular bond-

Table VI. Values of q_i and q_{ij} for Individual, Nonsymmetry VB Functions[a]

i	j	I	II	III	IV	V	VI	VII	VIII
1	1	0.9680	1.1042	0.0	0.0	0.0	0.0	0.0	0.0
	2	−0.0506	−0.0451	0.0	0.0	0.0	0.0	0.0	0.0
	3	−0.0062	−0.0063	0.0	0.0	0.0	0.0	0.0	0.0
	4	−0.0016	−0.0014	0.0	0.0	0.0	0.0	0.0	0.0
	5	−0.0062	−0.0063	0.0	0.0	0.0	0.0	0.0	0.0
	6	0.0966	−0.0451	0.0	0.0	0.0	0.0	0.0	0.0
2	2		0.9585	0.9187	1.0577	1.0544	0.9153	0.9194	1.0442
	3		0.0956	0.0947	−0.0452	−0.0523	0.0947	0.0968	−0.0464
	4		−0.0063	−0.0064	−0.0066	−0.0065	−0.0066	−0.0127	−0.0028
	5		−0.0009	−0.0018	−0.0008	−0.0013	−0.0012	−0.0002	−0.0008
	6		−0.0019	−0.0051	−0.0051	0.0057	−0.0023	−0.0028	0.0058
3	3			0.0645	0.9576	0.9672	0.9619	1.0153	1.1610
	4			−0.0514	0.0954	0.0985	−0.0536	−0.1116	−0.1103
	5			−0.0065	−0.0066	−0.0126	−0.0025	0.0001	−0.0035
	6			−0.0012	−0.0012	−0.0007	−0.0007	−0.0002	−0.0008
4	4			0.9720	0.9602	1.0189	1.1740	2.2482	2.2261
	5			0.0985	−0.0463	−0.1111	−0.1107	−0.1116	−0.1103
	6			−0.0126	−0.0028	0.0001	−0.0033	−0.0127	−0.0028
5	5			1.0198	1.1681	2.2396	2.2235		
	6			−0.1100	−0.1144	−0.1144	−0.1093		
6	6			2.1289	2.1234	1.1092	1.1154		

[a] The positions left blank can be determined from the symmetry and the other values.

not been written out. Since we have taken the σ orbitals to be doubly occupied in all configurations γ_σ is constant and the difference between the various VB functions is reflected in differences in the γ_{ij}'s. These numbers must satisfy the relation

$$\sum_{i,j} \gamma_{ij} S_{ij} = 6 \tag{3}$$

$$S_{ij} = \langle p_i | p_j \rangle \qquad S_{ii} = 1 \tag{4}$$

which is the number of π electrons, of course. As is well known, the quantities

$$q_i = \gamma_{ii} S_{ii} \tag{5}$$

$$q_{ij} = \gamma_{ij} S_{ij} + \gamma_{ji} S_{ji} \tag{6}$$

can be interpreted as the atomic and overlap charges, respectively. The sign and magnitude of the overlap charge determines the state of bonding between the two (in this case) orbitals. Thus, a large, positive value of q_{ij} indicates a strong bond between the respective atoms, and a large, negative value indicates strong antibonding. Table V gives the values of q_1, q_{12}, q_{13}, and q_{14} for the functions I* through VIII* and for the covalent only and covalent singly polar wave functions. For symmetry functions these give the independent values, of course. Upon examination of these numbers, it is seen that of all the individual VB basis functions III* has the largest bond order between adjacent

ing schemes. It is interesting to look at the q_i and q_{ij} for the individual bond functions also. These are given in Table VI for the functions I through VIII, which are, of course, not symmetry functions. A comparison of the q_{ij} for mutually ortho positions with the bonding diagrams shows that the prescription for writing the VB functions and the above bonding criterion based originally on properties of MO functions are certainly consistent in that the bonding diagrams show bonds in the same places as do the overlap charges. However, it is also seen that the bonds between adjacent atoms for all these functions are about the same order, varying only from 0.0947 to 0.0986. One of the largest of the bond orders is in the function III, but the appearance of the large ortho bond order in III* would not be expected from an examination of the q_{ij} for III. It is observed that III has one of the largest ortho antibonding orders, also. It might be expected that there would be some sort of cancelation between the bonding and antibonding effects in the ortho positions when the symmetry function is formed. Indeed, some such phenomenon appears to be operating in the transformation I → I*. However, in the case of III → III* there seems to be a synergistic effect between the charge separation and the bonding that prevents such cancelations, and in this case the ortho bonding is actually higher than any of the values in III. The exact nature of this phenomenon is not now clear, but its consequences

are clear in that III* provides by far the largest amount of overlap charge density of all the symmetry functions.[18]

One-Electron Terms in the Matrix Elements

Since we have worked out the first-order density matrices, these may be used to examine the behavior of the various VB functions with regard to the contributions of the kinetic energy, the nuclear attraction, and the repulsion between the σ electrons and the p_z orbitals. The electron repulsion within the π orbitals will be examined later. The atomic and overlap charge densities discussed in the last section may be used for this purpose. Thus, if we have

$$f_{ij} = \langle p_i | f | p_j \rangle \qquad (7)$$

$$F = \sum_i f_i \qquad (8)$$

we get, using (5) and (6)

$$\langle \psi | F | \psi \rangle = \sum_i q_i f_{ii} + \sum_{i<j} q_{ij} f_{ij}/S_{ij} \qquad (9)$$

These expressions work in this simple case since all the orbitals are real. Table VII gives the values of the

Table VII. Matrix Elements for p_z Orbitals

i	j	S_{ij}	T_{ij}/S_{ij}	$V(\text{nuc})_{ij}/S_{ij}$	$V(\text{core})_{ij}/S_{ij}$
1	1	1.00000	1.25159	-13.749	10.810
1	2	0.32004	0.32571	-12.504	10.164
1	3	0.07841	0.06937	-12.174	10.009
1	4	0.04417	0.00702	-12.172	10.052

independent matrix elements f_{ij}/S_{ij} for the kinetic energy and the nuclear attraction energy. In addition, the values of the pseudo-one-particle matrix elements $(2J_{\pi\sigma} - K_{\pi\sigma})_{ij}/S_{ij} = V(\text{core})_{ij}/S_{ij}$ are given in the table. The latter quantities are easily calculated from the two-electron integrals over AO's and the σ-core density matrix, viz.

$$V(\text{core})_{ij} = \sum_{rs} \{2[ij|rs] - [ir|js]\} \gamma(\text{core})_{rs} \qquad (10)$$

The energy corresponding to any of the VB functions may be written in the form

$$E(\psi) =$$
$$T_\pi + T_\sigma + V_\pi + V_\sigma + G_{\pi\pi} + G_{\pi\sigma} + G_{\sigma\sigma} + E_{\text{nuc}} \qquad (11)$$

where the subscripts give the source of the various contributions. For the functions that we have chosen with the σ electrons represented the same way at all times $T_\sigma + G_{\sigma\sigma} + E_{\text{nuc}}$ is a constant, and all the differences among the various functions arise from the π electrons. Table VIII gives values of T_π, V_π, $G_{\pi\pi}$, $G_{\pi\sigma}$, and $V_\pi + G_{\pi\pi} + G_{\pi\sigma}$ for each of the functions I*–VIII* and I–VIII. An examination of the entries in Table VIII shows no particular pattern to the numbers for either the individual VB functions or the sym-

(18) This effect cannot operate in the H_2 molecule since it requires the presence in the same function of both covalent and ionic type linkages. However, if one examines the VB function for describing two H_2 molecules simultaneously, it is found that a mixed polar–covalent function produces the largest overlap charge density of the individual symmetry functions, and the effect is nearly independent of the distance between the two molecules. Further publications on this point are planned.

Table VIII. Contributions to the Energy for Various VB Functions

	T_π	V_π	$G_{\pi\pi}$	$G_{\pi\sigma}$	$V_\pi + G_{\pi\pi} + G_{\pi\sigma}$
I*	7.2139	-82.0872	3.7085	64.6451	-13.7336
I	7.3533	-82.2827	3.7050	64.7486	-13.8291
II*	7.2590	-82.1552	3.7072	64.6827	-13.7653
II	7.5633	-82.9423	4.1848	64.7839	-13.9736
III*	6.5213	-81.1681	3.9300	64.1699	-13.0682
III	7.5302	-82.5248	3.9613	64.8757	-13.6878
IV*	6.7714	-81.5005	3.9923	64.3461	-13.1671
IV	7.7682	-82.8392	3.9488	65.0345	-13.8529
V*	7.1959	-82.0612	3.9664	64.6312	-13.4636
V	7.8775	-82.9925	4.0690	65.1191	-13.8044
VI*	7.1214	-81.9758	4.3379	64.5901	-13.0478
VI	7.8785	-82.9794	4.0607	65.1079	-13.8108
VII*	7.3424	-82.2746	4.1527	64.7470	-13.3749
VII	7.6329	-82.6767	4.1076	64.9590	-13.6101
VIII*	7.7757	-82.8569	4.0902	65.0500	-13.7167
VIII	8.1011	-83.3286	4.0893	65.3046	-13.9347
a	7.1974	-82.0724	3.7103	64.6396	-13.7225
b	6.4299	-81.0370	3.8484	64.0989	-13.0897

^{a} Values for covalent only function. ^{b} Values for covalent and singly polar function.

metry functions. Indeed, there appears to be a certain randomness present.

One of the most important principles that has been used in the qualitative discussion of VB bonding has been the idea that charge separation contributes to destabilization of a structure in which it occurs. The entries in Table VIII provide a test of this idea. If we consider an extremely naive model for a moment, it is seen that the numbers corresponding to ortho, meta, and para distances across the ring

$$1/r_{12} : 1/(\sqrt{3}r_{12}) : 1/(2r_{12}) = 0.3782 : 0.2183 : 0.1891 \text{ (au)}$$

should be proportional to the energy of charge separation in the ortho/meta/para singly polar VB functions as far as the potential energy is concerned. However, there is very little if any indication that such a mechanism is operating for these functions. There is perhaps a slight tendency for III and III* to have a more positive (less stable) value of $V_\pi + G_{\pi\pi} + G_{\pi\sigma}$ than the Kekule structure, but any effect of the sort under discussion appears to be largely masked by other more sizable phenomena.

The values of the electronic repulsion energy in the π shell do show a trend for the symmetry functions. Thus the structures with two electrons in one p_π orbital have higher energies than those for the covalent structures. However, the situation with the individual bond functions is different in spite of the fact that these VB functions might be expected to be simpler than the symmetry functions. Here the Dewar structure has the greatest repulsion energy.

When the actual diagonal matrix element of the energy is formed from these various contributions it is seen that there is some tendency for the differences to cancel, and these diagonal elements are reordered so that III* is the most stable with I* the next. This is the order of appearance in the wave function. It appears, therefore, that all attempts at approximate evaluation of the matrix elements of VB functions are likely to fail since the actual values and their importance are due to a rather delicate balancing of large terms. It may also be fairly noted that no mention of the size and importance of off-diagonal matrix elements has

been made. The natural feeling would, we believe, lead one to expect these to be even more difficult to estimate than the diagonal elements. This conclusion if it is indeed correct leads to considerable pessimism concerning the success of approximate or "semiempirical" VB calculations.

Finally, we call attention to the values for $G_{\pi\sigma}$. In semiempirical and approximate treatments the effect of the core is assumed to be constant for all the VB basis functions. As can be seen, these quantities vary fully as much as the other contributions to the matrix elements. Therefore, the assumption of a constant core–valence interaction, at least for the model considered here, is a severe oversimplification.

In this connection the exact effect of the form we have taken for the σ electrons may be questioned. The basic assumption is, of course, that the electron correlation in the σ shells makes no significant contributions to the way that the VB functions describe the correlation in the π shells. This could be tested by opening some of the σ MO's in the CI treatment, but we have not done this. Results of a rather different sort suggest, however, that the values of $G_{\sigma\pi}$ are quite insensitive to the nature of the σ orbitals. This is indicated by the fact that the use of the very minimal basis suggested by Christofferson[19] for the σ MO's gives very nearly the same values of $V(core)_{ij}/S_{ij}$. In this test Whitten's basis was still retained for the p_z orbitals, of course.

Resonance Energy Calculations

One of the early successes of the VB theory of benzene was the explanation of its extra stability over that predicted by the assumption of the additivity of empirical bond energies. This added stability was attributed to quantum mechanical resonance and hence was called the resonance energy. The method used by Pauling and Wheland to calculate the resonance energy was simply to find the difference between the energy of a single Kekule structure and the wave function I* + II*. This difference was expressed as 1.11α in terms of an unevaluated "exchange intergral" α. The comparison of several similar systems suggested the value of α to be approximately 32 kcal/mol. The result for benzene is a resonance energy of 36 kcal/mol. This calculation is easily duplicated with the ab initio values presented in this paper, and from Tables II and VII it is seen that the value of the resonance energy we obtain is 0.0493 au (30.9 kcal), somewhat lower than the semiempirical value.

However, Wheland[20] and Mulliken and Parr[21] criticized the above semiempirical results on the basis that the calculations were done at the experimental geometry of benzene and the empirical calorimetric resonance energies were obtained from energies of bonds at other internuclear distances. They pointed out that a "compression" energy of the bonds is involved if the calculations are performed at the benzene distances. When the compressional energy is included in the correct way, one obtains the "vertical" resonance energy of benzene to be 66 kcal/mol. This is a good bit higher

than the value arrived at above, and this fact also suggests that the covalent structures alone do not provide an adequate representation of the benzene molecule.

If indeed the covalent functions do not represent the benzene molecule in a satisfactory way, it seems necessary to devise a scheme for the calculation of the resonance energy that gives a more sophisticated description of the bonds in the molecule. Thus, within the framework that we are using we may attempt to use as a model of the hypothetical molecule with three isolated double bonds one in which some ionic character is built into the wave function. This has been done by determining the best wave function corresponding to resonance among the following bonding diagrams.
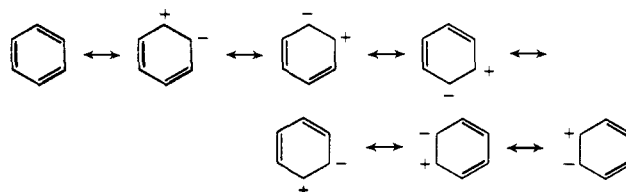
The energy for this wave function is -230.3395 au. When the hypothetical molecule with three isolated double bonds is represented in this way, the appropriate representation of the actual benzene molecule is the wave function consisting of all symmetry functions I* through VIII*. Substracting the two energies gives a resonance energy of 0.0978 au (61.4 kcal) which is in very satisfactory agreement with the experimental value of 66 kcal. Thus it appears that the ab initio calculation can provide an acceptable comparison with experiment if the model used is not too naive.

Conclusion

This article has given a description of an ab initio VB treatment of the π system of the benzene molecule. In the introduction two questions were asked. The first of these dealt with the problem of the nature of the difficulties of using the standard approximations in doing VB calculations. As we have seen, it appears that the main difficulty is the relative crudeness of these approximations as compared to the job they must do. One of these assumptions that has been made and which we have not yet mentioned is the neglect of orbital overlap. It is just this overlap that produces the variation among the various first-order density matrices of the VB functions, of course, and hence it appears that this overlap neglect is a significant contributer to the difficulties the approximate treatments have in matching the ab initio results.

The other question in the introduction dealt with the effects that the present results might have on the qualitative bonding theories used by experimental chemists. Any answer that we give for this question based as it will be upon the single example discussed in this article is extremely provisional. However, there is one quite suggestive fact which stands out in the calculation of the vertical resonance energy. There we saw that the inclusion of some ionic character in all of the bonds in a uniform way results in a highly improved calculated value. This suggests that the bonding diagram which is called the Kekule structure is better represented by

(19) R. E. Christofferson, D. W. Genson, and G. M. Maggiora, J. Chem. Phys., 54, 239 (1971).
(20) G. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955.
(21) R. S. Mulliken and R. G. Parr, J. Chem. Phys., 19, 1271 (1951).

the wave function including polar structures than by the single function I as has been past custom.

Pauling[22] has suggested that the so-called "resonance theory" of chemistry should be viewed as essentially empirical in nature and it "should not be identified with the valence-bond method of making approximate quantum-mechanical calculations of molecular wave functions and properties." We feel that the results of this article require that this question be reopened.

(22) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Section 6-5.

Although it may be true that many parts of chemistry will remain essentially empirical in nature, the general feeling on the part of most workers that the above identification could not be made in even simple cases may be the result of the inadequacies of the semiempirical approaches rather than due to inherent deficiencies in the model. Certainly, further work is required to settle these questions.

Localized *ab Initio* Analysis of an Electrocyclic Reaction

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Abstract: The origin of the stereospecificity of a concerted reaction is analyzed through an *ab initio* calculation. The method allows a distinction between the σ, π, and $\sigma\pi$ effects and confirms that the π electronic factors are responsible for the stereospecificity. In a localized approach, the main stereospecific contribution is the π delocalization energy between the π bonds as suggested in a previous demonstration. However, a stereospecific short range repulsion effect also appears, due to the overlap between the π bonds.

Quantum chemistry has brought a major contribution to the understanding of stereospecificity in electrocyclic reactions. The original demonstrations by Woodward and Hoffmann[1] and by Longuet-Higgins and Abrahamson[2] rely on very simple hypotheses and attribute the origin of the phenomenon to symmetry effects on the π system. Further contributions were mainly numerical, including the σ system, and tried to obtain reaction paths or the heights of reaction barriers.[3-5] In these numerical calculations it is difficult to locate the origin of the stereospecificity and to check the validity of the original theoretical demonstrations.

Both these demonstrations and numerical calculations deal with symmetry delocalized MO's, and symmetry considerations are often supposed to play the major role in the stereospecificity.[1,2,6] Alternative approaches have been proposed, using localized SCF orbitals.[7] In a preceding paper, a demonstration of the stereospecificity has been derived, using bond localized MO's and a perturbational development of the energy for the intermediate states.[8] The origin of the stereospecificity is attributed there to the π system, through a nth order delocalization contribution involving in a circular mode the n double bonds of the reacting circle. The validity of the hypothesis of this demonstration had been verified on the butadiene-cyclobutene reaction using the PCILO method[9] in the CNDO parametrization.[10] The present work tries to remove the restrictions of the previous study: namely (i) these calculations were semiempirical and *ab initio* calculations might behave differently, (ii) the perturbation was too strong in the transition state region and the perturbation series does not converge there. A variational procedure distinguishing π and $\sigma\pi$ factors and delocalization and correlation corrections has to be proposed.

I. Hypothesis

The calculation is performed in a minimal basis set of Slater atomic orbitals with optimized exponents ($\zeta_c(2s) = 1.759$, $\zeta_c(2p) = 1.670$, $\zeta_c(1s) = 5.679$, $\zeta_H = 1.227$). The atomic integrals are calculated using the POLYCAL program of Stevens.[11] The work is done in a basis of fully localized bond MO's. The nonorthogonal 1s MO's are simply the 1s AO's on the carbon atom. The σ nonorthogonal bond MO's are constructed from two hybrids in the valence shell satisfying the Del Re's criterion of maximum overlap;[12] these

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(12) G. Del Re, *Theor. Chim. Acta,* **1**, 188 (1963).