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References and Notes

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Ab Initio Valence-Bond Calculations. 5. Benzene

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Abstract: π-Electron ab initio valence-bond calculations for ground and singlet and triplet excited states of benzene have been performed using two minimal basis sets (STO, GTO). Vertical ionization potentials, atomization, and resonance energies have also been computed. By means of a population analysis the results have been interpreted and discussed in terms of individual and symmetry VB structures. Comparisons with previous semiempirical and ab initio calculations are presented.

1. Introduction

In a recent paper by Norbeck and Gallup[1] ab initio valence-bond (VB) results on benzene were interpreted as strongly different from those obtained by means of previous semiempirical treatments.[2,3] In particular, the question of the validity of the qualitative bonding theories commonly used by experimental chemists was raised. Our interest in performing a new VB calculation on benzene was to study to what extent the conclusions contained in that paper were dependent on the particular choice of the basis functions. To this aim we performed calculations using optimized Slater type orbitals (STO's) and a less sophisticated, but widely used basis set of Gaussian type orbitals (GTO's, ref 4). These two basis sets, in addition to the atomic SCF functions based on Gaussian lobes[5] used in ref 1, should be adequate to show up any dependence of the general results on the kind of basis functions used. It was also our interest to explore the capabilities of the VB method in studying the π-electron excited states (singlet and triplet) of such an important aromatic system as benzene, even when restricted to the use of a minimal basis set. The good agreement with experiment obtained for the ionization potentials (IP's) of H_2S[6] prompted us to perform theoretical calculations on the IP's of benzene. The next section briefly describes the method of calculation. Section 3 is concerned with the results obtained for the ground state; a comparison with the results of Norbeck and Gallup[1] is also given. In section 4 the results for the excited states and the ionization potentials are presented and discussed. General conclusions are contained in the last section.

Table I. Exponents for Basis Set Orbitals

Orbital	STO	GTO (STO-3G)[a]
$1s_H$	1.23	1.24
$1s_C$	5.68	5.67
$2s_C$	1.77	1.72
$2p_C$	1.68	1.72

[a] Reference 4.

Table II. Number of VB Structures Grouped According to the D_{6h} Symmetry Point Group

Symmetry	C_6H_6 singlet	C_6H_6 triplet	$C_6H_6^+$ doublet
A_{1g}	22	12	
A_{2g}	10	18	
B_{1g}			16
B_{2g}			19
E_{1g}			35
E_{2g}	30	30	
A_{1u}			16
A_{2u}			19
B_{1u}	16	18	
B_{2u}	13	15	
E_{1u}	27	33	
E_{2u}			35
Total no. of structures	175	189	210
Total no. of Slater determinants	400	225	300

2. Method of Calculation

(a) **Geometry and Basis Set.** The geometry reported in ref 7 has been used: r_{CC} = 2.6323 bohrs r_{CH} = 2.0409 bohrs, $\angle HCC = \angle CCC = 120°$ (regular hexagon). Two different minimal basis sets were used throughout the calculations: a set of STO's with exponents obtained optimizing the SCF energy of ethylene with the geometry reported in ref 7 (these exponents are very similar to those obtained by Stevens et al.[8] on benzene, using a slightly different geometry and another optimization criterion) and a set of GTO's contracted to the STO-3G basis of ref 4. The two basis sets are reported in Table I.

(b) **Method.** Only the six π electrons of benzene have been included explicitly in the VB calculations. The remaining 36 electrons have been confined in a "core" made of the lowest 18 σ-type SCF molecular orbitals. The influence of the potential provided by the σ "core" on the π electrons has been introduced, transforming the π one-electron Hamiltonian to an "effective" Hamiltonian according to the formula:[9]

$$\mathcal{H}_{pq}{}^{\text{eff}} = \mathcal{H}_{pq} + \sum_x \langle p|2J_x - K_x|q\rangle$$

where p and q are π basis functions; J_x and K_x are the usual Coulomb and exchange operators, the index x running over the occupied σ molecular orbitals. In this way the σ electrons no longer appear explicitly in the subsequent calculations and the VB problem reduces to that of six electrons and six ($2p_\pi$) orbitals. The "core" contribution to the electronic energy has been evaluated according to:[9]

$$E^{\text{core}} = 2\sum_x \mathcal{H}_{xx} + \sum_{x,y}(2J_{xy} - K_{xy})$$

where x and y run over the occupied σ SCF molecular orbitals. The VB calculations have been carried out by means of our program,[10-12] which makes direct use of canonical VB structures, with the same basis set used for the SCF calculation. The SCF-MO results for the two basis sets have been obtained using Univac adapted versions of Stevens (STO, ref 13) and Hehre (GTO, ref 14) programs, respectively.

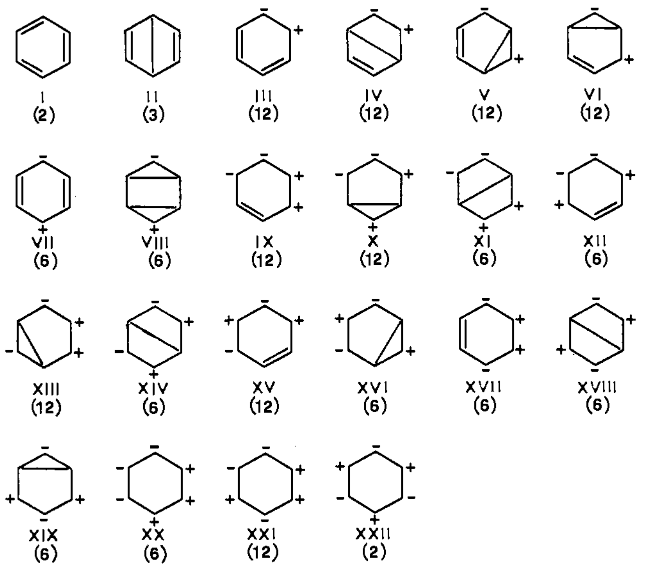

Figure 1. Canonical Rumer diagrams and number of equivalent individual structures for the ${}^1A_{1g}$ symmetry structures.

(c) **Calculations.** We performed full and limited VB calculations on singlet and triplet states of benzene and doublet states of the corresponding π cation using the two basis sets. In Table II, the number of symmetry structures belonging to the different irreducible representations of the D_{6h} point group are reported. In addition to the wave function, the energy, the structure occupation numbers, and the atomic and overlap charges have been computed.

3. Ground State

In Tables III-VIII we present results for the ground state of benzene for the two basis sets.

Inspection of Table III shows how the convergence toward the full VB result is obtained when adding different kinds of structures in the VB calculation.

It is interesting to point out that the chemical criterion to select the VB structures seems to work fairly well. In fact, when including all the structures with at least one covalent or two ionic bonds between adjacent atoms, provided no adjacent orbitals carry charge of the same sign (11 symmetry structures), 92 (STO) or 91% (GTO) of the basis set correlation energy is obtained. The basis set correlation energy is defined as the difference between the full VB and the SCF energies. The following points are noteworthy: the energy of the covalent structures (E_{cov}) is above the SCF value (E_{SCF}); the energy of the orthopolar structures alone (E_{ortho}) is below E_{cov} for both basis sets, in agreement with the results of Norbeck and Gallup,[1] but, contrarily to what found by them, E_{ortho} falls above the SCF value; the basis set correlation energy is smaller in ref 1 (0.08 hartree) than in both our calculations (0.10 hartree); the relative importance of the orthopolar structures with respect to the covalent ones is higher in ref 1 than in the present calculations when comparing E_{ortho}, E_{cov}, and the full VB result.

Table IV gives the energy values of each symmetry structure and the corresponding occupation numbers computed from the eigenvector of the full VB calculation (for the numbering of the structures, see Figure 1).

In agreement with Norbeck and Gallup,[1] a few important points emerge: the most stable symmetry structure is the orthopolar of type III (see columns 1 and 6 in Table IV); this is

Table III. SCF and VB Total Energies for Different Sets of $^1A_{1g}$ Symmetry Structures

	Symmetry structures	E, hartree[a]	E, hartree[b]	E, hartree[c]
Kekule	1	−230.2972	−230.077 809	−227.740 106
Kekule + Dewar	2	−230.3026	−230.084 216	−227.746 676
SCF	1	−230.3754	−230.215 126	−227.891 045
Orthopolar	2	−230.3781	−230.146 837	−227.803 636
Covalent + orthopolar	4	−230.4125	−230.250 715	−227.925 886
Singly polar	6		−230.196 832	−227.859 969
Covalent + singly polar	8	−230.4373	−230.280 901	−227.957 134
Covalent + singly + doubly polar	19		−230.314 875	−227.995 076
Full	22	−230.4546	−230.316 045	−227.996 452
Selected[d]	11		−230.308 015	−227.986 741

[a] Reference 1. [b] STO basis set. [c] GTO basis set. [d] Structures No. I, II, III, IV, V, VI, VII, XIV, XV, XVIII, and XXII (Figure 1).

Table IV. Diagonal Energies (E_i), Total Energy Variations (ΔE),[a] Variational Coefficients (C_i), and Occupation Numbers (n_i,n_i')[b,c] for $^1A_{1g}$ Symmetry Structures (full calculation)

Symmetry structure	STO basis set					GTO basis set				
	E_i, hartree	ΔE	C_i	n_i	n_i'	E_i, hartree	ΔE	C_i	n_i	n_i'
1	−230.077 809	3.92	0.2803	0.222	0.174	−227.740 106	4.27	0.2832	0.222	0.165
2	−230.063 167	1.03	0.1426	0.110	0.047	−227.725 321	1.12	0.1442	0.110	0.044
3	−230.104 576	13.67	0.2804	0.251	0.297	−227.758 867	15.96	0.2838	0.252	0.303
4	−229.992 289	4.51	0.1450	0.117	0.115	−227.641 248	5.21	0.1481	0.118	0.116
5	−229.684 348	2.12	0.0830	0.042	0.052	−227.327 558	2.39	0.0847	0.041	0.051
6	−229.661 537	1.82	0.0761	0.038	0.044	−227.304 500	2.09	0.0783	0.038	0.043
7	−229.568 333	1.38	0.0641	0.023	0.032	−227.213 266	1.55	0.0656	0.023	0.032
8	−229.438 990	0.24	0.0241	0.007	0.006	−227.084 652	0.28	0.0250	0.007	0.006
9	−228.926 802	0.03	0.0062	0.001	0.000	−226.558 371	0.04	0.0074	0.001	0.001
10	−229.001 546	0.15	0.0149	0.003	0.003	−226.633 977	0.20	0.0162	0.003	0.003
11	−228.565 886	0.01	0.0025	0.000	0.000	−226.200 355	0.01	0.0027	0.000	0.000
12	−229.205 856	0.75	0.0353	0.012	0.014	−226.837 327	0.95	0.0383	0.013	0.015
13	−228.989 146	0.11	0.0126	0.002	0.002	−226.621 880	0.15	0.0140	0.003	0.002
14	−229.198 716	0.58	0.0303	0.009	0.011	−226.833 263	0.72	0.0327	0.009	0.012
15	−229.793 473	5.65	0.1437	0.086	0.097	−227.431 987	6.68	0.1457	0.085	0.100
16	−229.347 992	1.26	0.0479	0.016	0.025	−226.980 324	1.44	0.0494	0.015	0.025
17	−229.211 798	0.57	0.0309	0.011	0.011	−226.843 279	0.75	0.0342	0.011	0.012
18	−229.413 408	1.60	0.0564	0.021	0.032	−227.046 437	1.88	0.0586	0.021	0.033
19	−229.346 708	1.16	0.0460	0.015	0.023	−226.978 795	1.34	0.0476	0.015	0.023
20	−228.083 656	0.00	−0.0001	0.000	0.000	−225.703 600	0.00	0.0000	0.000	0.000
21	−228.946 537	0.10	0.0121	0.003	0.001	−226.563 714	0.14	0.0137	0.003	0.002
22	−229.308 756	0.66	0.0350	0.010	0.012	−226.934 230	0.76	0.0359	0.009	0.012

[a] Total energy increase when eliminating the *i*th structure from the full calculation in kilocalories per mole. [b] $n_i = C_i^* \Sigma_j C_j S_{ij}$ (ref 15); S_{ij} is the overlap integral between structures *i* and *j*. [c] $n_i' = |C_i^2|/(S^{-1})_{ii}$ (ref 16); $(S^{-1})_{ii}$ is the *i*th diagonal element of the inverse overlap matrix.

Table V. Diagonal Energies (E_i) and Occupation Numbers (n_i, n_i') for Individual VB Structures (full calculation)

	STO basis set			GTO basis set		
	E_i, hartree	n_i[a]	n_i'[b]	E_i, hartree	n_i[a]	n_i'[b]
Kekule	−230.038 514	0.111	0.087	−227.701 198	0.111	0.083
Dewar	−229.975 706	0.037	0.016	−227.638 699	0.037	0.015
Orthopolar[c]	−229.669 046	0.021	0.025	−227.318 732	0.021	0.025

[a] $n_i = C_i^* \Sigma_j C_j S_{ij}$ (ref 15). [b] $n_i' = |C_i|^2/(S^{-1})_{ii}$ (ref 16). [c] Orthopolar of type III (Figure 1).

also the most contributing structure to the wave function (see columns 3, 4, 5 and 8, 9, 10); the increase in energy when eliminating the orthopolar symmetry structure of type III from the full VB calculation (see columns 2 and 7) give the same indication. At this point, we want to call attention to the fact that all these results are based on the use of symmetry structures: in this way the considerations on the relative importance of the different VB structures are directly connected to, and might be dependent on, the degree of symmetry present in the molecule. In fact, when examining the energy values and the occupation numbers for individual structures reported in Table V, the indication is that now the Kekule structure is the most important, in agreement with that commonly expected. It is also interesting to analyze the overlap charges computed for different individual structures (Table VI): a covalent bond between adjacent atoms (i, j) has practically the same degree of bonding ($q_{ij} \simeq 0.1$) in any kind of structure; summing all the q_{ij}'s for each individual structure, the Kekule structure

Table VI. Overlap Charges in Individual and $^1A_{1g}$ Symmetry Structures[a]

	Kekule[b]	Dewar[b]	Orthopolar[b]	Kekule[c]	Dewar[c]	Orthopolar[c]
			Individual Structures			
q_{12}	0.10153	−0.04857	−0.10716	0.09097	−0.04374	−0.09545
q_{23}	−0.05088	0.10135	0.10287	−0.04557	0.09084	0.09203
q_{34}	0.10153	−0.04857	−0.05111	0.09097	−0.04374	−0.04573
q_{45}	−0.05088	−0.04857	0.10023	−0.04557	−0.04374	0.08992
q_{56}	0.10153	0.10135	0	0.09097	0.09084	0
q_{61}	−0.05088	−0.04857	0	−0.04557	−0.04374	0
Σq_{ij}	0.15195	0.00842	0.04483	0.13620	0.00672	0.04077
			Symmetry Structures			
q_{ij}	0.03818	0.03275	0.13647	0.03802	0.03272	0.13187

[a] $q_{rs} = \gamma_{rs}S_{rs} + \gamma_{sr}S_{sr}$; γ_{rs} = (r,s) element of the charge density matrix; S_{rs} = overlap integral between orbitals r and s; orbitals are numbered counterclockwise starting from the top vertex (Figure 1). [b] STO basis set. [c] GTO basis set.

Table VII. Atomic and Overlap Charges for Different Sets of $^1A_{1g}$ Symmetry Structures Based on STO's[a]

	Symmetry structures	q_{11}	q_{12}	q_{13}	q_{14}
Covalent	2	0.9602	0.0426	−0.0027	−0.0004
Orthopolar	2	0.8542	0.1517	−0.0038	−0.0043
Covalent + orthopolar	4	0.8608	0.1449	−0.0044	−0.0026
Singly polar	6	0.8297	0.1768	−0.0031	−0.0070
Covalent + singly polar	8	0.8406	0.1657	−0.0035	−0.0056
Covalent + singly + doubly polar	19	0.8122	0.1949	−0.0038	−0.0067
Full	22	0.8110	0.1962	−0.0038	−0.0068
Selected[b]	11	0.8193	0.1876	−0.0036	−0.0065

[a] $q_{rr} = \gamma_{rr}S_{rr}$; see Table VI, footnote *a*. [b] See Table III, footnote *d*.

Table VIII. Atomic and Overlap Charges for Different Sets of $^1A_{1g}$ Symmetry Structures Based on GTO's[a]

	Symmetry structures	q_{11}	q_{12}	q_{13}	q_{14}
Covalent	2	0.9639	0.0383	−0.0021	−0.0003
Orthopolar	2	0.8639	0.1409	−0.0031	−0.0034
Covalent + orthopolar	4	0.8677	0.1370	−0.0037	−0.0020
Singly polar	6	0.8392	0.1662	−0.0025	−0.0057
Covalent + singly polar	8	0.8485	0.1567	−0.0029	−0.0045
covalent + singly + doubly polar	19	0.8195	0.1864	−0.0031	−0.0054
Full	22	0.8181	0.1878	−0.0032	−0.0055
Selected[b]	11	0.8271	0.1786	−0.0030	−0.0052

[a] $q_{rr} = \gamma_{rr}S_{rr}$; see Table VI, footnote *a*. [b] See Table III, footnote *d*.

results the overall most binding one; the overlap charges over individual Kekule and orthopolar structures are in perfect agreement with those reported in ref 1.

The bottom row of Table VI shows the overlap charges obtained with wave functions represented by Kekule, Dewar, and orthopolar symmetry structures. The interesting result here is that, in analogy with that found for the energy (Table III) and in very good agreement with the results reported in ref 1, the symmetry orthopolar structure turns out to be the most binding one.

We attempt an explanation of these results on the basis of the following considerations: each symmetry structure is a linear combination of many individual VB structures which do overlap and interact; in particular, the Kekule and the orthopolar symmetry structures are combinations of two and 12 individual structures, respectively; the solution of the symmetry problem is equivalent to a variational calculation based on the individual VB structures related by the symmetry operations of the point group; the answer of a variational calculation is dependent both on the nature and the number of the basis functions introduced.

At this point, according to us, the results presented in this paper and those reported in ref 1 concerning the relative importance of the symmetry structures should be considered quite understandable and reasonable. The results obtained including five covalent and 24 orthopolar individual structures (rows 2 and 4 in Table III) are also quite understandable and reasonable on the basis of these considerations.

A general comment on the interpretation of the VB wave function by means of the occupation numbers seems worthwhile (Table IV). In fact, owing to the nonorthogonality of the structures, in the VB theory there is no unique way of defining the weight of the structures in the wave function. We have reported, in addition to the variational coefficients C_i, two different kinds of normalized occupation numbers: $n_i = C_i^*\Sigma_j C_j S_{ij}$,[15] $n_i' = |C_i|^2/(S^{-1})_{ii}$,[16] where S_{ij} is the overlap integral between structures i and j, and $(S^{-1})_{ii}$ is the ith diagonal element of the inverse overlap matrix. Only n_i' are positive definite quantities, so that they are theoretically more satisfying even if their interpretation is less evident. The values of C_i, n_i, n_i' can be significantly different (see also ref 16); C_i and n_i seem to give an estimate of the importance of the

Table IX. Resonance[a] and Atomization[b] Energies

	STO	GTO	Exptl
E_{res}[c]	28.7	28.5	66[d]
E_{res}[e]	67.4	69.3	
$E_{\mathrm{at}}^{\mathrm{SCF}}$	1.918	1.901	2.099[f]
$E_{\mathrm{at}}^{\mathrm{VB}}$	2.019	2.007	

[a] In kilocalories per mole. [b] In hartree. [c] This is the classical resonance energy defined as the difference between the energy of an individual Kekule structure (Table V) and the energy corresponding to all covalent structures (Table III). [d] Empirical value obtained from experimental data (see ref 1). [e] This is the resonance energy with inclusion of orthopolar structures as defined in ref 1. [f] Reference 21.

Table X. Singlet π-Electron Spectrum of Benzene[a]

Symmetry state	ΔE[b]	ΔE[c]	ΔE[d]	ΔE[e]	ΔE[f]
B_{2u}	5.31	5.39	5.26	4.89	4.9
E_{2g}	8.75	8.89	8.62	6.14	6.2
B_{1u}	10.45	10.78	9.48	6.76	6.98
E_{1u}	11.48	11.77	10.61	8.18	7.3
A_{1g}	13.20	13.46	12.67	8.89	
A_{1g}	13.54	13.81	13.13	10.36	
E_{2g}	14.97	15.34	13.78	10.69	

[a] ΔE are in electron volts. [b] STO basis set. [c] GTO basis set. [d] Gaussian lobes basis set: ref 18. [e] Experimental values reported in ref 18. [f] Experimental values reported in ref 19.

structures close to that given by the sequence of the structure energies; on the other hand, according to ref 16, n_i' should be more related to the increase in energy when eliminating the ith structure from the full VB matrix, but exceptions appear in our results (Table IV).

However, C_i, n_i, and n_i' all agree in predicting the orthopolar symmetry structure as the most relevant, even if in a less dramatic way in the case of C_i and n_i.

Tables VII and VIII give atomic and overlap charges for a number of calculations corresponding to different sets of symmetry structures. The agreement between the results obtained for the two basis sets is again satisfactory. It is worth pointing out that the convergence toward the full VB result and the validity of the chemical criterion for choosing the relevant VB structures seem to parallel the conclusions drawn from the results concerning the total energy (Table III).

In Table IX, atomization and resonance energies are reported. The VB atomization energy, in both basis sets, is in quite better agreement with experiments than the SCF value.

The computed resonance energy, when classically defined, turns out in poor agreement with the empirical value. Following Norbeck and Gallup,[1] we have also computed the resonance energy, including the effect of the orthopolar structures. In this way, a very good agreement with the empirical value is reached (see ref 1). However, the important role played by the concept of resonance energy rests exclusively, in our opinion, on its semiquantitative basis and, according to us, it is not worth the effort of looking for a more sophisticated theoretical model.

4. Excited States and Ionization Potentials

In this section, we report the data concerning the excited singlet and triplet π-electron states of benzene (Tables X and XI). In addition, the computed vertical π IP's of benzene are shown (Table XII).

Table XI. Triplet π-Electron Spectrum of Benzene[a]

Symmetry state	ΔE[b]	ΔE[c]	ΔE[d]	ΔE[e]	ΔE[f]
B_{1u}	3.96	4.01	3.98	3.66	3.9
E_{1u}	5.53	5.63	5.39	4.69	4.7
E_{2g}	7.52	7.63	7.48	5.76	5.6
B_{2u}	9.44	9.73	8.61	5.96	6.55
B_{1u}	11.42	11.58	11.34	8.36	

[a] ΔE are in electron volts. [b] STO basis set. [c] GTO basis set. [d] Gaussian lobes basis set: ref 18. [e] Experimental values reported in ref 18. [f] Experimental values reported in ref 19.

Table XII. Vertical Ionization Potentials[a]

Symmetry state	STO[b]	GTO[b]	GTO[c]	Expt[d]	Expt[e]
$^2E_{1g}$	8.38	7.98	9.21	9.25	9.3
$^2A_{2u}$	11.36	11.00	12.01	11.49	11.8
$^2E_{2u}$	14.15	13.84	14.64	12.3	12.5
$^2E_{2u}$	15.36	15.10	15.55		
$^2A_{1u}$	16.70	16.46	16.70		
$^2A_{2u}$	17.17	16.91	17.42		
$^2B_{2g}$	17.38	17.13	17.66		
$^2B_{1g}$	17.49	17.25	17.74		

[a] IP = $E(C_6H_6^+) - E(C_6H_6)$, in electron volts. [b] Present work. [c] Reference 19. [d] Reference 20. [e] Reference 22.

In performing these calculations, we assumed the core electrons frozen in the same SCF-MO's used for the ground state; this choice has already been made by Hay and Shavitt[19] in a large basis set configuration interaction (CI) calculation on benzene and by us[6] in the context of a VB calculation of the IP's of H_2S.

Tables X and XI show the same kind of agreement with experiments obtained by similar full CI calculations on the minimal basis set.[18] Interesting indications come from the analysis of the various states. The $^1B_{2u}$ state is described up to 90% by a combination of Kekule and orthopolar symmetry structures of type III (Figure 1) in a relative ratio similar to that of the ground state. The next state, $^1E_{2g}$, has predominantly a Dewar character with smaller contributions from the corresponding orthopolar structures (type IV). The $^1B_{1u}$ state is still more ionic in character with significant contributions from structures of type XV, III, VII, V, VI (in decreasing order). The next states are described in terms of many different structures of higher ionicity. It seems important to emphasize that the Kekule structures contribute significantly only to the first excited state of benzene ($^1B_{1u}$). From an analysis of the ground and excited states of triplet benzene, it is found that the most important structures are those deriving from the Kekule and orthopolar structures of type III, where a covalent bond is broken and the two unpaired electrons are on adjacent atoms; a contribution comes also from the structures of type IV, were the long bond has been broken and the unpaired electrons are in 'para' positions.

The π IP's reported in Table XII are in satisfactory agreement with the assignment made by Price et al.,[20] but in disagreement with the interpretation given by Hay and Shavitt of their theoretical results.[19] According to Price, in fact, the experimental values at 9.25 and 11.49 eV are to be assigned to the ionization of the two π orbitals of benzene with no σ IP's interposed. Hay and Shavitt,[19] instead, interpret the two peaks at 9.25 and 12.3 eV as arising from the ionization of π orbitals and assign the peak at 11.49 eV to a σ ionization, in agreement with the SCF calculations. The present results are not accurate enough to support Price's assignments; VB calculations including σ electrons would be able to give a more definite answer to the question of the interpretation of the photoelectron spectrum of benzene, which has still to be considered open.

5. Conclusions

From a numerical point of view, our results show substantial agreement with those of Norbeck and Gallup.[1] In particular, we want to emphasize the comparison of our results in Table VI with those in Table V and VI of ref 1.

The trend in overlap charges for Kekule and orthopolar symmetry structures in both calculations are very similar, as are the contributions of these structures to the wave function. Almost perfect agreement between the two calculations is obtained in the case of individual structures.

The results here obtained using two different basis sets (STO, GTO) are in good agreement between themselves: this is particularly encouraging for VB calculations on molecular systems bigger than benzene owing to the drastic reduction in computing time allowed by the use of GTO basis sets.

Our analysis shows the importance of considering separately the indications coming from calculations based on individual structures and those based on symmetry structures. It turns out, in fact, that the individual Kekule structure is the most stable and the most binding; in addition, its occupation number in the full VB ground-state wave function is the highest. Moreover, a given amount of "binding strength" (expressed as overlap charge) can be assigned to a covalent bond between adjacent atoms appearing in a canonical Rumer diagram practically independently of the kind of structure. The results based on symmetry structures show the importance of the resonance among equivalent structures (related by symmetry operations of the point group of the molecule). It turns out that the resonance between the two Kekule structures is less effective than that among the 12 orthopolar structures as far as the ground-state energy and the charge overlap matrices of benzene are concerned. The chemical criterion for selecting structures to be included in limited VB calculations seems to work as well as in the case of more localized systems.[6,12,17,23]

The analysis of the wave functions of the lowest singlet and triplet excited states of benzene together with that of the benzene cation (doublet states) gives a further indication that the structures with the highest number of covalent bonds are the most contributing.

Our final conclusion is that the qualitative picture given by simple theories of the chemical bond in delocalized systems as benzene are not in disagreement with the results of our VB ab initio calculations.

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