excited states, although the first term in eq 1 and the higher excited states should not be neglected for the larger molecules having more closely spaced electronic states.

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Ab Initio SCF Computations on Benzene and the Benzenium Ion Using a Large Contracted Gaussian Basis Set

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Abstract: Improved SCF computations on the benzene molecule and especially the benzenium ion (protonated benzene), using a large contracted gaussian basis set including polarization functions, are presented. The results for the benzenium ion are consistent with the conventional model of a $C_5H_5^+$ structure with an attached CH_2 group, the whole somewhat modified and stabilized by hyperconjugation. The calculations predict the equilibrium HCH angle at the protonated carbon atom to be 103.5° and that the distance to the adjacent carbon atom is lengthened by 0.055 Å. The proton affinity is found to be 189 kcal/mol as compared with an experimental value of 183.1. One-electron properties are compared with corresponding benzene values, and changes at the ring positions are discussed. A population analysis for both σ and π (and quasi-π) overlap populations and charges is reported and discussed. From the overlap populations in the ring bonds, it is estimated that the lateral C-C bonds are shortened by 0.015 Å, and the C-C bonds para to the CH_2 group are lengthened by 0.020 Å, as compared with benzene.

In 1954 Muller, Pickett, and Mulliken[3] published some semiempirical π-electron-only SCF calculations bearing on the question of hyperconjugation (HCJ) in $C_6H_7^+$, that is, protonated benzene. Allowance for charge reorganization in the σ-electron framework was made by use of the so-called ω technique. When the authors made these relatively crude calculations, they looked forward to the day when a good all-electron SCF calculation could be made.

From the results of these calculations, estimates of the contribution of HCJ to the stabilization energy of $C_6H_7^+$ (in the free state, of course, whereas experimental observations[4] are mostly in solution) yielded values which depended on the assumed values of the semiempirical parameters used. However, with a fairly reasonable choice of parameters ($\omega = 1.4$ for charge redistribution and $\delta = -0.2$ for electronegativity of hydrogen vs. carbon), a vertical HCJ energy of 21 kcal/mol was obtained, or a net HCJ energy of 14 kcal/mol after allowing for changes in bond length as a result of HCJ.

Empirical evidence[5] has led organic chemists to assume a localized model (see Figure 1) for $C_6H_7^+$ in which five carbon atoms (2-6 in Figure 2) form a semi-aromatic $C_5H_5^+$ structure, while the sixth ring carbon (1 in Figure 2) is bound in an essentially aliphatic CH_2 group with its plane perpendicular to the ring (symmetry C_{2v} if the ring remains planar). However, an examination of HCJ resonance structures (Figure 1) shows two groups of structures which are hyperisovalent; that is, the number of π plus quasi-π bonds is the same in both. The one group of structures has full benzene aromaticity: two Kekule (plus three Dewar) structures each having three π bonds, with the plus charge on the H_2. The other group of three structures has the plus charge on the C_5H_5 with the CH_2 neutral; here there are two π and one quasi-π bonds. One expects stronger HCJ in such an isovalent case than occurs in the case of sacrificial HCJ (see Figure 1 for an example of the latter)[6] and, in ref 3, it was argued that, as a result, the aromatic character of the benzene ring would be present to a considerable extent in $C_6H_7^+$. However, the empirical evidence, and, it may be said here, the results of the present computation, indicate that this partial preservation of the aromatic character of the ring, through HCJ, while certainly present, is less important than suggested in ref. 3.

Rather recently,[7] Hehre and Pople have carried through an all-electron SCF computation on the benzenium ion. In most of their computations, they used a minimal basis set

(STO3G). In terms of this, they established the C_{2v} model as being considerably more stable than one in which, instead of its being part of a CH_2 group, the added proton is located between two of the ring atoms. In their calculations, they assumed the ring of carbon atoms to lie in a plane, with the same distances as in C_6H_6 for the five carbon atoms 2-6 and the three hydrogen atoms 3-5. The remaining geometrical parameters were allowed to vary, and the geometry at which the computed energy was minimized was established. Finally, an energy computation was made with a larger basis set (4-31G) for the geometry which minimized the energy.

We thought that a comprehensive calculation using a still larger basis set, including polarization functions, would be worthwhile and might give an improved understanding of the role and importance of HCJ, and we have carried out such a computation. We assumed C_{2v} symmetry and assumed that the carbon atoms all lie in a plane, with the same C-C and C-H distances as in benzene for carbons 2-6. We varied the C_1C_2 and C_1C_6 distances and the HCH angle in the CH_2 and determined the configuration of minimum computed energy. From a population analysis, we have estimated the departure of the conformation of the atoms C_2 to C_6 from our initial assumptions; these departures are small. We have not sought to determine whether all the carbon atoms C_1-C_6 actually lie in a plane; Hehre has expressed the opinion[8] that the ring may be slightly puckered. However, a slight puckering would make only very minor changes in the results reported here.

Figure 2 shows: (a) our numberings of the atoms and the *assumed* bond lengths for the C-C and C-H bonds involving carbon atoms 2-6 and also the assumed lengths for the C-H bonds in the CH_2 group; (b) the *results* of our computations on the C_1-C_2 and C_2-C_6 bond lengths (1.45 Å) and the HCH angle in CH_2 (103.5°). The latter may be compared with the Hehre and Pople minimal basis set results of 1.472 Å and 105.3°.

The present paper on the benzenium ion is intended as a prelude to similar, further work on the methylated benzenium ions beginning with toluenium. These ions are of high interest because each substituted methyl group increases the basicity of benzene with specific effects depending on the location of this group. A qualitative explanation in terms of HCJ has been given,[9] followed by π-electron-only semiempirical SCF calculations by Ehrenson.[10] Recently, minimum basis set calculations on toluenium and other monoalkyl substituted benzenium ions have been briefly reported by Hehre et al.[11]

Calculations

The ab initio self-consistent field calculations for the benzene molecule and the benzenium ion ($C_6H_7^+$) were done using basis sets comprised of contracted gaussian-type functions (CGTF's). The carbon (11s 7p) and hydrogen (7s) optimized atomic basis sets of van Duijneveldt[12] were augmented with single d- and p-type polarization functions having exponents of 0.9 for C and 1.1 for H. The exponents and contraction coefficients for the carbon and hydrogen centered GTF basis sets are listed in Table I. The full basis set for $C_6H_7^+$ contains 298 primitive and 162 contracted GTF's and may be represented symbolically as (11s 7p 1d/7s 1p)/[5s 3p 1d/3s 1p].

A nine-point potential energy surface was generated for $C_6H_7^+$ by varying the C_1-C_2 internuclear distance and the $H_1C_1H_7$ angle as shown in Figure 2. The C_1-H_1 and C_1-H_7 distances were fixed at 1.0975 Å (a value intermediate between the C-H bond lengths in benzene and ethane), and the remaining C-C and C-H distances and CCC and HCC bond angles were assumed to retain the corresponding benzene values of 1.395 Å, 1.085 Å, and 120°. The nine points were obtained by using three C_1-C_2 distances of 1.395, 1.4675, and 1.54 Å and three $H_1C_1H_7$ angles of 90°, 109°28′, and 120°. A tenth point was computed at the equilibrium geometry as determined from the original nine-point surface.

The molecular integrals were computed using the PO-

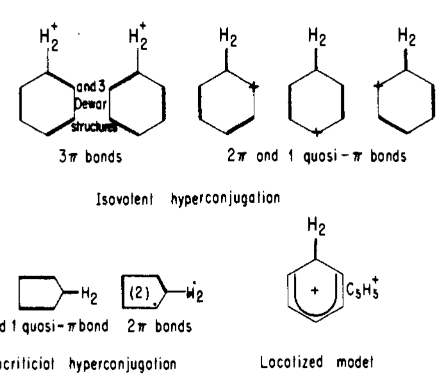

Figure 1. Examples of hyperconjugation in aromatic molecules.

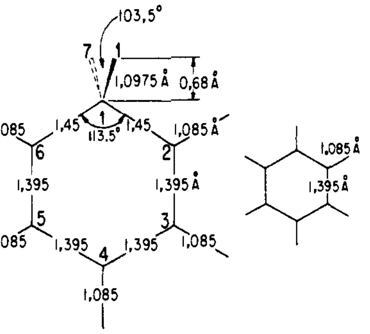

Figure 2. Benzenium geometry. Angle $H_1C_1H_7$ and distance $R(C_1C_2) = R(C_1C_6)$ were varied; other dimensions were assumed to be as in benzene.

Table I. (11s 7p 1d/7s 1p)/[5s 3p 1d/3s 1p] Basis Set of Gaussian-Type Functions Used in Calculations on Benzene and the Benzenium Ion

Atom	Type	Exponent	Coefficient
Hydrogen	s_1	188.614448	0.001747
		28.276596	0.013503
		6.424880	0.069212
		1.815041	0.266068
		0.591063	0.732318
	s_2	0.212149	1.0
	s_3	0.079891	1.0
	p_1	1.1	1.0
Carbon	s_1	15469.4	0.000569
		2316.47	0.004419
		527.099	0.022914
		149.438	0.092116
		48.8562	0.290778
		17.6209	0.678086
	s_2	6.81082	0.645574
		2.72760	0.389214
	s_3	0.75674	1.0
	s_4	0.30073	1.0
	s_5	0.11409	1.0
	p_1	51.7233	0.004339
		12.3397	0.030121
		3.77224	0.128247
		1.32487	0.361507
		0.50546	0.616496
	p_2	0.19827	1.0
	p_3	0.07731	1.0
	d_1	0.9	1.0

Table II. Two-Electron Integrals for the Benzenium Ion Due to a (11s 7p 1d/7s 1p)/[5s 3p 1d/3s 1p] Gaussian Basis Set

Stage	Atoms	Contracted basis functions	Unique non-zero integrals (for C_{2v})	Integrals $>10^{-6}$ (for $R_{C_1C_2}$ = 1.395 Å, $\angle H_1C_1H_7$ = 109°28′)
1	C_2–C_6, H_2–H_6	1–130	10169353	6401465 (1)
2	C_1 and with above	131–150	7633436	5051826 (4)
3	H_1, H_7 and with above	151–162	5797483	3148714 (10)
Totals:	$C_6H_7^+$	162	23600272	14602005

Table III. Potential Energy Surface for the Benzenium Ion

Point	$R_{C_1-C_2}$, Å	$\angle H_1C_1H_7$, deg	E, hartrees
1	1.395	109.47	−231.0696
2	1.395	120.00	−251.0618
3	1.395	90.00	−231.0703
4	1.4675	109.47	−231.0769
5	1.4675	120.00	−231.0719
6	1.4675	90.00	−231.0719
7	1.54	109.47	−231.0621
8	1.54	120.00	−231.0594
9	1.54	90.00	−231.0524
10	1.45	103.5	−231.0784

Table IV. Energy Quantities (in hartrees) for Benzene and the Benzenium Ion

Energy	Benzene	Benzenium (Pt 10)
Total (E)	−230.7771	−231.0784
Kinetic (T)	230.4661	230.8666
Nuclear attraction	−943.7509	−951.3565
Electron repulsion	279.0682	277.8628
Nuclear repulsion	203.4394	211.5487
Binding[a]	1.6557	1.9570
Virial ratio ($-E/T$)	1.0013	1.0009
ϵ_{23} ($1e_{2u}$, $2a_2$)[b]	0.119	−0.068
ϵ_{22} ($1e_{2u}$, $3b_1$)[b]		−0.183
ϵ_{21} ($1e_{1g}$, $1a_2$)	−0.337	−0.546
ϵ_{20} ($1e_{1g}$, $2b_1$)		−0.640
ϵ_{19} ($3e_{2g}$, $7b_2$)	−0.496	−0.699
ϵ_{18} ($3e_{2g}$, $11a_1$)		−0.715
ϵ_{17} ($1a_{2u}$, $1b_1$)	−0.501	−0.811
ϵ_{16} ($3e_{1u}$, $6b_2$)	−0.589	−0.794
ϵ_{15} ($3e_{1u}$, $10a_1$)		−0.800
ϵ_{14} ($1b_{2u}$, $5b_2$)	−0.621	−0.842
ϵ_{13} ($2b_{1u}$, $9a_1$)	−0.644	−0.863
ϵ_{12} ($3a_{1g}$, $8a_1$)	−0.710	−0.922
ϵ_{11} ($2e_{2g}$, $4b_2$)	−0.825	−1.038
ϵ_{10} ($2e_{2g}$, $7a_1$)		−1.062
ϵ_9 ($2e_{1u}$, $3b_2$)	−1.016	−1.230
ϵ_8 ($2e_{1u}$, $6a_1$)		−1.254
ϵ_7 ($2a_{1g}$, $5a_1$)	−1.152	−1.375
ϵ_6 ($1b_{1u}$, $4a_1$)	−11.236	−11.437
ϵ_5 ($1e_{2g}$, $2b_2$)	−11.236	−11.437
ϵ_4 ($1e_{2g}$, $3a_1$)		−11.449
ϵ_3 ($1e_{1u}$, $2a_1$)	−11.238	−11.488
ϵ_2 ($1e_{1u}$, $1b_2$)		−11.488
ϵ_1 ($1a_{1g}$, $1a_1$)	−11.238	−11.495

[a] Relative to the separate atomic energies computed using the same basis set ($E_C = -37.6869$; $E_H = -0.5000$). [b] Lowest unoccupied MO's.

LYATOM programs,[13] which were modified[14] to take full advantage of the assumed C_{2v} symmetry of $C_6H_7^+$ in that only symmetry-unique (nonredundant) basis function integrals were computed and processed. The two-electron integrals were generated in such a way that only those that would be affected by the geometry changes were recomputed. Hence, integrals involving basis functions centered only on the atoms C_2, C_3, C_4, C_5, C_6, H_2, H_3, H_4, H_5, and H_6 (Figure 2) were computed once, those involving basis functions centered on C_1 four times, and those involving basis functions centered on H_1 and H_7 ten times. The number of symmetry-unique two-electron integrals and the number of these that were actually saved (based on a 10^{-6} threshold), to be processed at the SCF stages of the calculations, are listed in Table II. The numbers of two-electron integrals shown in column 4 of Table II were computed for point 1 only; thereafter, for the remaining points, the numbers listed in column 5 were computed. Since point 1 has the shortest C_1–C_2 distance (1.395 Å), it was assumed that integrals less than 10^{-6} for this point would not become larger for the remaining points, which have longer C_1–C_2 distances. The savings in computational effort may be gauged by comparing the figures shown in Table II with the number of two-electron integrals that would have been generated if the contractions, the C_{2v} symmetry, the three stages, and the smallness threshold were not employed. A basis set consisting of 298 primitive GTF's yields 992418076 two-electron integrals and subsequent contraction of this basis set to 162 CGTF's reduces this number to 87166206.

The energies computed in the ten calculations described above are presented in Table III. The equilibrium geometry (point 10) was obtained from a two-dimensional harmonic fit of points 1-9.

Various total energy quantities and molecular orbital energies for benzene and the benzenium ion at its theoretically determined equilibrium geometry are listed in Table IV. Each orbital energy is labeled according to the corresponding D_{6h} (C_6H_6) and C_{2v} ($C_6H_7^+$) irreducible representations.

Expectation values of selected one-electron operators centered at the symmetry-unique C and H atoms and at the center of the C_6H_6 ring were computed using the benzene and the equilibrium geometry benzenium ion wave functions. Population analyses[15] were also carried out for each of these wave functions.

Discussion

Perhaps the best way to gauge the quality of theoretical computations is to make comparisons with existing experimental data. Unfortunately, the only such quantity available for the benzenium ion is the proton affinity of benzene. Recent ion cyclotron resonance measurements[16] have placed the PA of benzene at 183.1 kcal/mol, whereas earlier mass spectrometric determinations[17] yielded 183 ± 3 kcal/mol. The present computed result of 189.1 kcal/mol differs by about 3% from these values and is in close agreement with the value of 187.9 reported in ref 7 for their 4-31G basis set.

In the case of benzene, values of the deuteron quadrupole coupling constants and the molecular quadrupole moment have been determined experimentally. The electric field gradients, in atomic units (au), derivable from the observed[18] deuteron quadrupole coupling constants, are q_{aa} = 0.143, q_{bb} = 0.132, and q_{cc} = −0.275, each having a reported uncertainty of about 0.002. These may be compared with the corresponding values from Table V of 0.168, 0.144, and −0.312. Similarly, we obtain a value of −6.916 au for the molecular quadrupole moment of benzene, which may be compared with an experimentally determined value[19] of −4.16 ± 2.08 au.

Although it appears that the discrepancies between theory and experiment are somewhat large, it should be noted that an earlier study[20] of the basis-set dependence of these properties indicated that the inclusion of polarization functions is important for the approach of the theoretical field gradients toward the experimental values. The molecular quadrupole moment was calculated to be close to −7 au for all basis sets considered except a minimal set in which the p exponents were constrained to be the same for the σ and π directions, where the value was more than a factor of 2 smaller. These two properties, one sampling the charge distribution in the region of the nuclei and the other reflecting the charge distribution over the entire molecule, are reasonable probes of the quality of the wave functions. The fact that the present calculations approach the experimental values suggests that the wave functions are close to the SCF basis set limit in quality.

The total and orbital energies computed for benzene in the present study are in close agreement with those reported in ref 20. The use of more extensive atomic basis sets accounts for the additional energy depression of −0.0277 au below that of ref 20. The polarization functions produced energy lowerings of about 0.1 au in both the present and in the ref 20 calculations. Hence, the energy due to the [5s 3p 1d/3s 1p] CGTF basis set is within 0.04 au of the estimated[20] Hartree–Fock limit energy.

The properties reported in Table V have been listed in terms of their respective nuclear, σ, and π or quasi-π contributions in order to facilitate a comparison of the changes produced at the ortho, meta, and para positions in the benzenium ion and with the corresponding values for the benzene molecule. One general trend noteworthy in Table V is that the most pronounced effects of protonation on the one-electron properties are evidenced in those centered at the carbon nuclei. This suggests that the added proton has taken on the character of a C-H bond similar to the original six hydrogens. The values of the individual H-centered properties are all perturbed somewhat from the corresponding values in benzene, but the values do not differ greatly for the positions 1-7 in the benzenium ion.

This relation is found to hold even for the electric field gradients, which are rather sensitive probes of the charge distribution near a nucleus. The angles $\phi(\mathrm{H})$, which define the principal axis system, deviate by less than 1° from the bond axes. There is a noticeable effect on the π contributions to the values of $\mathbf{q}(\mathrm{H})$ in that the values at the meta positions are close to the corresponding benzene values, whereas the ortho and para π contributions are quite different. Since these contributions are small compared with the σ portions, the total values of $\mathbf{q}(\mathrm{H})$ are not much affected.

The charge densities at the carbon and hydrogen nuclei [$\langle\langle\delta(\text{r-C})\rangle$, $\langle\delta(\text{r-H})\rangle$] and the nuclear-electron potentials [$\Phi(\mathrm{C})$, $\Phi(\mathrm{H})$] show similar trends in that the (small) π contributions to the property exhibit the strongest effects both with regard to the ring positions and in comparison with the benzene values.

The values of $\mathbf{q}(\mathrm{C})$ are the most interesting because large changes are evident in the values at the C_1-C_4 positions. It has been observed that there is a correlation between the relative magnitudes of electric field gradients and intramolecular charge transfer and, consequently, a relationship to a population analysis.[21] Table V shows that the values of the electric field gradients in the π direction (q_{aa}) in the benzenium ion have the values 0.019, 0.780, 0.280, and 0.889 au at carbons 1-4. One characteristic of electric field gradients is that a buildup of positive charge around a nucleus leads to increased values.[21] The value of $q_{aa}(\mathrm{C})$ in benzene is 0.376. The protonation, therefore, causes a drastic decrease in charge around C_1 and a small decrease in charge around the meta carbons (C_3 and C_5). The ortho and para carbons have increased values of q_{aa} relative to benzene, suggesting an increase of positive charge. The value of $q_{aa}(C_4)$ is greater than $q_{aa}(C_2)$, indicating a greater positive charge at the para position and, possibly, increased importance of the hyperquinoid resonance structure shown in Figure 1. Note also that the π contributions account for most of these effects. The population analysis (Figure 3) is in qualitative agreement with these trends.

Table V. One-Electron Properties of Benzene and the Benzenium Ion Centered at the Symmetry-Unique Carbon and Hydrogen Nuclei[a]

Property	C_6H_6	$C_6H_7^+$ (1)	$C_6H_7^+$ (2)	$C_6H_7^+$ (3)	$C_6H_7^+$ (4)
q_{aa} (C)	0.376	0.019	0.780	0.280	0.889
	−0.978	−0.581	−0.943	−0.974	−0.976
	2.322	1.998	2.370	2.314	−2.444
	−0.968	−1.398	−0.065	−1.060	−0.578
q_{bb}(C)	−0.232	0.018	−0.418	−0.102	−0.463
	0.688	0.392	0.560	0.692	0.689
	−1.380	−1.112	−0.730	−1.312	−1.416
	0.460	0.738	0.312	0.518	0.265
q_{cc}(C)	−0.144	−0.038	−0.362	−0.179	−0.426
	0.290	0.189	0.383	0.282	0.287
	−0.942	−0.886	1.080	−1.002	−1.027
	0.508	0.660	0.355	0.542	0.314
ϕ(C)			−17.660°	−0.448°	
q_{aa}(H)	−0.168	−0.153	−0.148	−0.166	−0.143
	−0.959	−0.834	−0.960	−0.959	−0.959
	0.765	0.570	0.780	0.797	0.787
	0.026	0.111	0.032	0.023	0.029
q_{bb}(H)	−0.144	−0.133	−0.144	−0.133	−0.146
	−0.727	−0.730	−0.714	−0.726	−0.728
	0.513	0.473	0.526	0.520	0.535
	0.071	0.123	0.044	0.073	0.047
q_{cc}(H)	0.312	0.286	0.292	0.299	0.289
	1.686	1.563	1.674	1.686	1.687
	−1.277	−1.056	−1.307	−1.290	−1.322
	−0.097	−0.221	−0.076	−0.096	−0.076
ϕ(H)		−13.395°	−0.189°	−0.113°	
$\langle\delta(\text{r-C})\rangle$	122.543	122.367	122.705	122.502	122.741
	0.0	0.0	0.0	0.0	0.0
	122.543	122.367	122.705	122.502	122.741
	0.0	0.0	0.0	0.0	0.0
$\langle\delta(\text{r-H})\rangle$	0.446	0.412	0.438	0.434	0.436
	0.0	0.0	0.0	0.0	0.0
	0.446	0.208	0.438	0.434	0.436
	0.0	0.204	0.0	0.0	0.0
Φ(C)	−14.729	−14.513	−14.483	−14.528	−14.478
	9.745	9.900	9.918	9.869	9.855
	−22.467	−22.191	−22.500	−22.461	−22.557
	−2.008	−2.221	−1.901	−1.936	−1.776
Φ(H)	−1.104	−0.855	−0.888	−0.912	−0.880
	9.342	9.846	9.546	9.454	9.438
	−9.143	−8.770	−9.141	−9.114	−8.972
	−1.304	−1.931	−1.290	−1.252	−1.345

[a] All property values are in atomic units. The numbers in parentheses in columns 3–6 indicate the particular C or H atom at which the property is centered (see Figure 2). C_6H_6 and $C_6H_7^+$ are situated with the carbon atoms in the *yz* plane and C_1, H_1, and H_7 in the *xz* plane. The origin of coordinates is the center of the C_6H_6 ring, and C_1 lies along the positive *z* axis. The electric field gradient tensors have been rotated to their principal axis coordinate systems as defined by the angle ϕ, which corresponds to the deviation from the respective C–H bond directions. The aa, bb, and cc components correspond to the xx, yy, and zz components, respectively, in the case of C_6H_6. The components for $C_6H_7^+$ are correlated to those for C_6H_6. The four entries for each property correspond to the total and its breakdown in terms of nuclear, σ, and π contributions.

The other components of the carbon-centered electric field gradients also show marked differences, most of which can also be attributed to the contributions from the π MO's. The rotation angle $\phi(C_2)$ is seen to be deviated by 17.7° from the C_2H_2 bond direction, whereas the small value of $\phi(C_3)$ = 0.4° indicates that the changes at the meta position are considerably smaller.

Finally, we report in Table VI expectation values of powers of the coordinates. The four values listed for each property have the same significance as described in Table V. The changes associated with these origin-centered properties are indications of the changes in the overall charge dis-

Table VI. Expectation Values of Powers of Coordinates with Origin at the Center of the Benzene Ring[a]

Property	C_6H_6	$C_6H_7^+$
R^{-1}	0.161	0.379
	14.936	15.016
	−12.722	−12.682
	−2.053	−1.956
R	0.0	0.493
	0.0	4.732
	0.0	−0.559
	0.0	−3.680
R^2	−78.019	−57.819
	381.973	405.694
	−398.766	−391.284
	−65.226	−72.229
X^2	−30.617	−26.458
	0.000	5.306
	−15.614	−17.039
	−15.003	−14.724
Y^2	−23.701	−17.627
	190.986	190.987
	−189.576	−186.203
	−25.111	−22.410
Z^2	−23.701	−13.736
	190.986	309.401
	−189.576	−188.042
	−25.111	−35.095

[a] The four entries for each property correspond to the total and its breakdown in terms of nuclear, σ, and π contributions. All entries are in atomic units.

tribution when a proton is added to benzene. The electronic ($\sigma + \pi$) contribution ($\langle r^2 \rangle$) to R^2 is seen to decrease slightly from 464.0 to 463.5 au due to a combined increase in the π and decrease in the σ terms. Hence, the benzenium molecule seems to be, overall, about the same size as benzene. The greater value of $\langle z^2 \rangle$ for benzenium (223.1 vs. 214.7 au) indicates that the π MO's have skewed the charge density in the (positive) z direction.

Comparing benzenium with benzene in Table IV, corresponding ϵ's are all increased in the latter, obviously because of the added nuclear charge of the proton. Further, the degeneracies of the e_1 and e_2 MO's of benzene are split, with the b_1 component for e_{1g} or e_{2u}, or the a_1 component for e_{2g} or e_{1u}, being the lower in benzenium. The downward shifts are largest for the b_1 MO's of benzenium, which are π or quasi-π MO's involved in HCJ. The $1a_2$ MO is also a π MO but is not involved in HCJ; its form (see Table VII) is almost unchanged in benzenium as compared with benzene.

In benzene, the most tightly bound π MO $1a_{2u}$ has about the same energy as the nearest σ MO's ($3e_{2g}$) but, in benzenium, the energy of the corresponding π MO ($1b_1$) is now decisively lower, a result which must be attributed to hyperconjugative action. In fact, it is now slightly lower even than the next lower σ MO's $6b_2$ and $10a_1$.

From the coefficients in Table VII and corresponding coefficients for the σ MO's, a population analysis was made in the usual way,[15] although experience has shown that such analyses must be taken with a few grains of salt. The π populations in Figure 3 are especially relevant to the matter of hyperconjugation. Included with the π orbitals is the quasi-π orbital formed by essentially the linear combination 1s–1s of the 1s AO's on the H atoms of the CH_2 group. The π-overlap populations, indicated by the encircled numbers at the left, are an index of the strengths of π bonding among the various atoms. The relatively large overlap population (0.662) in the quasi-π bond from C to H_2 in $C{=}H_2$ is a reflection of the fact that this bond is much stronger than ordinary π bonds.

Table VII. π and Quasi-π Molecular Orbital Coefficients[a]

		Benzene			Benzenium			
		$1a_{2u}$	$1e_{1g}$	$1e_{1g}$	$1b_1$	$1a_2$	$2b_1$	
E, hartrees		−0.501	−0.337	−0.337	−0.811	−0.546	−0.640	
H_1, H_7	s				±0.199		±0.095	
	s				±0.093		±0.076	
	s				±0.028		±0.078	
	px	0.004		0.008	∓0.007		∓0.003	
	py					+0.003		CH_2
	pz				∓0.012		∓0.005	
					B		B	
C_1	px	0.202		0.302	0.388		0.147	
	px	0.120		0.213	0.225		0.104	
	px	0.027		0.092	0.037		−0.060	
	dxz	0.012		−0.010	0.014		0.014	
	dxy		0.020			0.016		
		B		B	B		A	
C_2, C_6	px	0.202	0.261	0.151	0.122	0.254	−0.103	
	px	0.120	0.184	0.107	0.057	0.185	−0.073	
	px	0.027	0.079	0.046	0.004	0.058	0.005	
	dxz	−0.006	−0.013	0.013	0.003	−0.015	0.017	
	dxy	−0.010	−0.002	−0.013	−0.010	−0.002	−0.001	
		B	B	A	B	B	B	
C_3, C_5	px	−0.202	0.261	−0.151	0.070	0.275	−0.250	
	px	0.120	0.184	−0.106	0.040	0.204	−0.169	
	px	0.027	0.079	−0.046	0.004	0.060	−0.047	$C_5H_5^+$
	dxz	0.006	0.013	0.013	0.005	0.014	−0.003	
	dxy	−0.010	−0.002	0.013	−0.010	−0.005	0.015	
		B			B		B	
C_4	px	0.202		−0.302	0.053		−0.277	
	px	0.120		0.213	0.030		−0.176	
	px	0.028		−0.092	0.002		−0.021	
	dxz	0.012		−0.010	0.005		−0.016	
	dxy		0.020			0.022		
H_2, H_6	px	0.004	0.007	0.004	±0.002	±0.005	∓0.002	
H_3, H_5	px	0.004	0.007	−0.004	±0.001	±0.006	∓0.005	
H_4	px	0.004		−0.008	0.001		−0.005	

[a] Relative to the CGTF's listed in Table I. Bonding and antibonding interactions between fragments are denoted by B and A, respectively.

Table VIII. Overlap Populations between Carbon Atoms

	Benzene			Benzenium		
Atoms[a]	Total	σ	π	Total	σ	π
C_1–C_2	0.981	0.664	0.317	0.618	0.543	0.075
C_2–C_3				1.086	0.708	0.378
C_3–C_4				0.851	0.624	0.227
C_1–C_3	−0.164	−0.135	−0.029	−0.063	−0.072	0.009
C_2–C_4				−0.100	−0.115	0.015
C_2–C_6				−0.201	−0.145	−0.056
C_3–C_5				−0.156	−0.135	−0.021
C_1–C_4	−0.043	0.008	−0.051	−0.016	−0.023	0.007
C_2–C_5				−0.016	0.015	−0.031

[a] See Figure 2.

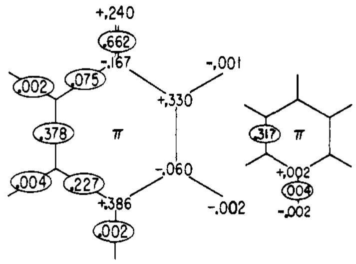

Figure 3. π and quasi-π charges and overlap populations (encircled) in benzenium ion and benzene, omitting C_1C_3, C_1C_4, H_1H_7, etc. overlap terms.

The overlap population between the CH_2 carbon and its carbon neighbors is a measure of the hyperconjugative interaction between the CH_2 and the $C_5H_5^+$. It is not negligible, but not impressively strong. On the other hand, the lateral π bonds in the $C_5H_5^+$ part of the molecule (C_2–C_3 and C_5–C_6) are stronger than in benzene, but the π bonds (C_3–C_4 and C_4–C_5) to the bottom C atom are weakened.

The overlap populations between carbon atoms in benzene and the benzenium ion are listed in Table VIII. The entries for *adjacent* atoms are shown in Figures 3, 5, and 6, but are also included in the table for completeness. The σ and π overlaps between carbon atoms and their second nearest neighbors are seen to all be antibonding, while those for the third nearest neighbors are small and antibonding or slightly bonding in benzenium. The overlap populations C_2–C_6 and C_3–C_5 indicate, when compared with the corresponding value in benzene, that the two bonds C_2–C_3 and C_5–C_6 should be slightly nonparallel in the benzenium ion. The fact that the differences are small tends to reinforce our decision to keep the C_2–C_3–C_4–C_5–C_6 skeleton frozen in its benzene configuration for the benzenium ion study. A more conspicuous change is seen in the C_1–C_3 overlap populations. The decrease in antibonding character there is consistent with the corresponding increase in the bonding interaction between C_2 and C_3.

The charge distribution is also of interest. Most of the positive charge is concentrated on three carbon atoms in ortho-para style, but there is a fair amount in the H_2 part of the CH_2. However, this is largely balanced by a strong negative charge on the CH_2 carbon atom. The distinctly larger computed plus charge on carbon 4 than on carbon 2 and 6 in Figure 3 suggests that the hyperquinoid resonance structure for benzenium in Figure 1 is of special importance.

A better idea of the π-electron distribution can be obtained by looking at the forms of the three π MO's which are involved. Their coefficients and orbital energies are indicated in Table VII, along with the corresponding data for benzene. Corresponding to the nondegenerate a_{2u} MO of benzene is the $1b_1$ of benzenium. The MO is now seen to extend throughout the CH_2 group and, in fact, forms an important part of the bonding of the C to the H_2 within the latter. At the same time, there is bonding, symbolized by the letter B, from the CH_2 group to the rest of the ring. At other places in the diagram, the letter B or A has been placed to indicate bonding or antibonding, respectively, between the atoms concerned. The ± coefficients for H_1 and H_7 refer to the signs of the H atom basis functions of the CH_2 group (the + sign for H_1 which lies above the ring plane and overlaps the + part of the carbon π AO's, and the − sign for H_7 which lies below the plane and overlaps the − part of the carbon π AO's). Correspondingly, the overlap populations between H_1 and H_7 are −0.069 (total), 0.055 (σ), and −0.124 (π), indicating that the small σ-bonding interaction between H_1 and H_7 is twice as small as the π-antibonding interaction. It is seen that there is a considerable amount of hyperconjugation bonding in $1b_1$ as indicated by the product of the coefficients on C_1 and on C_2 and C_6. However, the $1b_1$ MO is seen to be *primarily* a CH_2 MO.

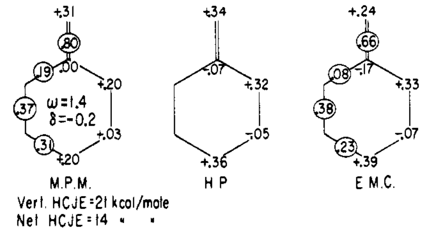

Figure 4. π and quasi-π charges and overlap populations (encircled) for benzenium ion due to three wave functions (see text).

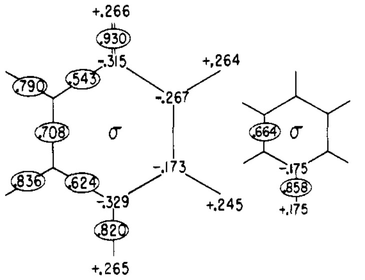

Figure 5. σ charges and overlap populations (encircled) in benzenium ion and benzene, omitting C_1C_3, C_1C_4, H_1H_7, etc. overlap terms.

The degenerate $1e_{1g}$ MO in benzene splits in benzenium into $1a_2$ and $2b_1$. The $1a_2$ is seen to be almost identical in benzene and benzenium, and to be localized on the ring except for some very small polarization terms. The $2b_1$, on the other hand, which is primarily a $C_5H_5^+$ MO (though differing considerably from its benzene counterpart) extends also into the CH_2. However, the overlap with the CH_2 is antibonding thus making a negative contribution to the hyperconjugation energy. On the other hand, it makes a positive contribution to bonding within the CH_2 group.

Thus $1b_1$ and $2b_1$ together contribute to quasi-π bonding within the CH_2 group and to π bonding within the $C_5H_5^+$ group and, in addition, give some net hyperconjugation bonding between the two groups.

Figure 4 compares the results for the π populations with those of previous papers.[3,7,22] The present results do not differ much from those of Hehre and Pople, except in respect to the charge distribution in the CH_2 group. Qualitatively they are similar to the early results of Muller et al., but hyperconjugation is much smaller, and the positive charge, which there favored the CH_2 group, is now mostly shifted to the C_5H_5 group.

Figure 5 shows the results of a population analysis of the σ-charge distribution and Figure 6 of the total ($\sigma + \pi$) pop-

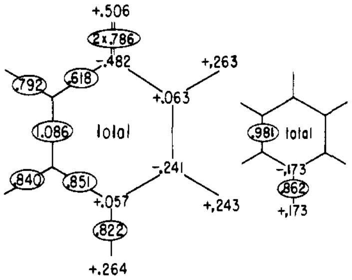

Figure 6. Total charges and overlap populations (encircled) in benzenium ion and benzene, omitting C_1C_3, C_1C_4, H_1H_7, etc. overlap terms.

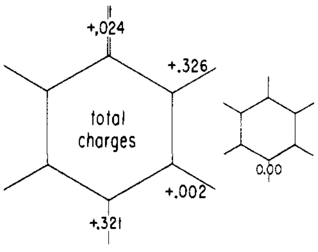

Figure 7. Gross atomic charges for benzenium ion and benzene.

ulation, in comparison with benzene. Figure 7 analyzes the total charges in terms of the CH_2 group as a whole and of the CH groups of the rings, each as a whole. Comparing Figures 5 and 6 with Figure 3, the relative strengths of the C_2–C_3 and C_5–C_6 bonds as compared with the C_3–C_4 and C_4–C_5 and especially the C_1–C_2 and C_2–C_6 bonds are seen to be repeated and reinforced in the σ as in the π bonds. The quasi-σ is seen to be considerably stronger than the quasi-π bond within the CH_2 group; however, the sum of the two (Figure 6) is about the same as for two C–H bonds of nearly the same strength as the CH bonds of the ring atoms. The overall charges in the CH groups taken as a whole show (Figure 7) a simple pattern with the total plus charge of the ion concentrated symmetrically on CH groups 2, 4, and 6.

By interpolation and extrapolation of the relations between bond lengths in Figure 2 and overlap populations in Figure 6, one can estimate that, as compared with the *assumed* values in Figure 2, the C_2–C_3 and C_5–C_6 bonds are shortened in the benzenium ion to about 1.38 Å and the C_3–C_4 and C_4–C_5 bonds lengthened to about 1.415 Å. Similarly, using the data in Table VIII, the C_2–C_6 distance is predicted to increase by 0.006 Å, while the C_3–C_5 distance is unchanged.

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