rather small sets of F 1s and S 2p ΔBE's being a bit more accurately described. The *formally* more well-grounded approach of eq 5 thus offers little practical improvement over the eq 1 method, and the deficiency of CNDO for these systems is still obvious.

But one further possibility may be considered here. This is noticed if one examines eq 4 and 5; in both equations the *relative* weights of the local charge contribution (K_Aq_A) and the other-atom contribution (V) are fixed. Notice further that in the approach of eq 1, the local charge contribution is adjusted *via* the parameter k, while the other-atom contributions in V always get their full unit weight. Both observations suggest that one might more accurately describe the ΔBE's by letting both the local- and other-atom contributions be adjustable in the form

$$\Delta\text{BE} = aq_A + bV + c \qquad (6)$$

Of course q_A and V are not independent variables since the sum of the charges in the system (q_A and all q_B) must equal the net charge (zero for all cases here); but inasmuch as the CNDO theory is approximate and we seek "empirical" relationships, the approach merits examination. (The older atomic-charge-only correlations[2-4] are a special case of eq 6 if $b = 0$ is required.) Fits according to eq 6 are also summarized in Table II, the results being similar to eq 5 applications. Only the calculated F 1s and S 2p ΔBE's are essentially more accurate than before, but these cases fit just four and five pieces of data, respectively, with three adjustable parameters, and we should really look at larger data sets to make proper comparisons.

We conclude with two remarks. First, if CNDO is to be used for ΔBE's, one should focus attention on families of closely related molecules[8] and try the more rigorous potential approaches of eq 4 and 5 or the more flexible adjustment of eq 6. Second, there is a need for more accurate valence electron description by approximate MO schemes and other MO schemes should be considered[10] in connection with ΔBE's.

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XV. The Protonation of Benzene

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Contribution from the Laboratoire de Chimie Théorique,[1b] *Université de Paris-Sud, Centre d'Orsay, 91 Orsay, France, and the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.* *Received January 13, 1972*

Abstract: Simple *ab initio* molecular orbital theory is applied to the study of the possible geometries and energies of protonated benzene. Using the STO-3G minimal basis set the optimum form of the ion is found to be one in which the proton is bonded to a ring carbon which assumes approximately tetrahedral coordination. The form in which the proton bridges a carbon-carbon bond is found to be less favored, and structures corresponding to edge and face protonation are found to be poorer still. The calculated proton affinity of benzene is in good agreement with experiment, and a theoretical value is proposed for the energy required for the proton to migrate from one carbon to another through a bridged intermediate.

In previous papers in this series we have considered the application of *ab initio* molecular orbital theory to the study of the electronic structure of simple organic molecules and ions. We extend our applications now to consider the species $C_6H_7^+$, the ion formed upon the protonation of benzene.[2] This system is interesting and warrants special consideration primarily because it and ions of similar type have long been implicated in processes of electrophilic aromatic substitution. Any structural information derived theoretically on this ion could in principle lead to a more thorough understanding of the possible mechanisms of such reactions. A further motive for this research is to enable us to test whether or not the structure for protonated benzene resembles to any extent the structures of simpler carbocations, in particular the ethyl cation. It is likely that any serious direct attempt to elucidate the transition states involved in aromatic substitution reactions by *ab initio* methods can only be carried out realistically on model systems.

It must be cautioned at the outset that the results of our technique, as well as the majority of others that have been applied to this problem, should really be compared only with experimental measurements performed on the dilute gas. We make no pretense of understanding at this time the effect of solvent media on the structure and energetics of ionic species, and hope only that the model we present might be useful as a starting point for detailed treatments of such effects.

Quantum Mechanical Method

We have applied single-determinant *ab initio* molecular orbital theory throughout. Unless otherwise specified, a minimal basis set of functions closely related to Slater-type orbitals is used. In this basis (STO-3G), each atomic function is replaced by a least-squares-fitted sum of three Gaussian functions. These are associated with the standard molecular set of expo-

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[1] (a) National Science Foundation Postdoctoral Fellow 1971-1972. (b) The Laboratoire de Chimie Théorique is also part of the Laboratoire de Physico-Chimie des Rayonnements, associated with the CNRS.

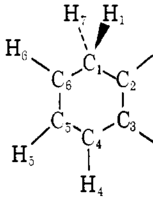
[2] For a recent review see G. A. Olah, *Accounts Chem. Res.*, 4, 240 (1971), or for a more classical treatment, A. Streitwieser Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 11.

nents proposed elsewhere.[3a] In addition to the STO-3G calculations, a small number of studies have been carried out with the extended 4-31G basis.[3b] This has a set of four Gaussian inner shell functions, but the valence functions are split into inner (three Gaussian) and outer (one Gaussian) parts. This basis has proved superior for energy comparisons[4] but is too large to be practical for numerous studies of molecules of the size considered in this paper.

Protonation of Benzene

For neutral benzene (point group D_{6h}) we have used the standard molecular geometry proposed in paper I of this series[5,6] (r_{CC} = 1.40 Å and r_{CH} = 1.08 Å). To find suitable structures for protonated benzene, we have performed partial geometry optimization at the STO-3G level on each of two forms. We have also considered briefly two additional types of structure but have found these to be extremely unfavorable. We now comment in detail.

In the first structure the general C_{2v} geometry I was



I

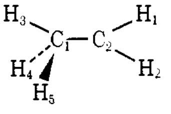
assumed, together with the further constraint that the carbon skeleton C_2–C_3–C_4–C_5–C_6 and the hydrogens H_3,H_4, H_5 were fixed in the same positions as in the standard model for benzene. The remaining parameters, varied until the energy was minimized, are as follows.

$r(C_1H_1)$ = 1.106 Å $\quad\alpha = \angle C_2C_1C_6 = 110.9°$

$r(C_2H_2)$ = 1.094 Å $\quad\beta = \angle H_1C_1H_7 = 105.3°$

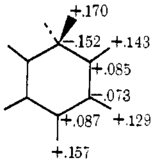
$r(C_1C_2)$ = 1.472 Å $\quad\angle H_2C_2C_3 = 118.3°$

We note that the $C_6C_1C_2$ angle (α) has closed down from 120° in neutral benzene to nearly the tetrahedral value, resulting in a lengthening of the C_1C_2 bond from 1.40 Å (in benzene) to 1.472 Å. Also noteworthy is the fact that the structure we report here closely parallels a previously published geometry for the eclipsed form of the ethyl cation.[7] In this study a carbon–carbon bond length of 1.488 Å was found (using the STO-3G basis), much the same as the value reported here, and angles $H_3C_1C_2$ = 112.9° and $H_4C_2H_5$ = 105.9° (structure II) were directly analogous to values for α and β, respectively, in benzenium.[8]

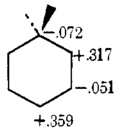


II

STO-3G total atomic charges, calculated within the Mulliken framework,[9] are also of some interest (IIIa).



IIIa



IIIb

These show charge alternation similar to that found in many neutral systems[10] (aromatic and aliphatic alike) and a surprisingly heavy concentration of negative charge on the protonated carbon. Ring π charges (IIIb) show identical but somewhat larger effects.

Two other all-electron calculations on a structure of this form for protonated benzene have previously appeared in the literature.[11,12] Both employ wave functions based on the CNDO method, and both have reached conclusions similar to ours about the geometry of the ion. It should be mentioned, however, that Jakubetz and Schuster report their structure to be a saddle point (rather than a minimum) on the $C_6H_7^+$ potential surface. The structure we report is a minimum and the lowest energy form of $C_6H_7^+$ that we have located.

This type of structure for protonated benzene with a roughly tetrahedral site of protonation is favored by numerous infrared,[13] ultraviolet,[14,15] and nuclear magnetic resonance[16] studies on protonated aromatics in solution. (The solution nmr spectra of protonated benzene itself has only recently been reported by Olah, Schlosberg, Kelly, and Mateescu.[17]) Also it is consistent with the recent crystal structure for the tetrachloroaluminate salt of the heptamethylbenzene cation.[18] There appear to have been no structural measurements made on this or related species in the gas phase.

A second structure considered (with C_s symmetry) is one in which the proton bridges a carbon–carbon bond (IV–V). Again we have partially optimized the molecular geometry[19] using the STO-3G basis, constraining as before part of the nuclear framework (skeletal car-

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(3) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

(4) See, for example, W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(5) J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967).

(6) It might be mentioned that the optimum STO-3G geometry for this molecule gives bond lengths within 0.01 Å of these values: M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(7) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(8) We adopt the nomenclature proposed by Olah and coworkers [G. A. Olah, **94**, 808 (1972), and references therein], terming the *classical* tricoordinate ion (I) benzenium and the *nonclassical* species (IV) benzenonium.

(9) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(10) W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970); (b) W. J. Hehre, L. Radom, and J. A. Pople, *ibid.*, **94**, 1496 (1972).

(11) E. Heglstand, *Acta Chem. Scand.*, **24**, 3687 (1970).

(12) W. Jakubetz and P. Schuster, *Angew. Chem., Int. Ed. Engl.*, **10**, 497 (1971).

(13) H. H. Perkampus and E. Baumgarten, *Ber. Bunsenges. Phys. Chem.*, **68**, 70 (1964).

(14) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

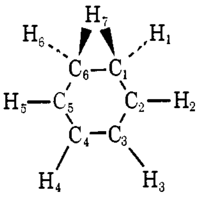
(15) G. Dallinga, E. L. Mackor, and A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

(16) C. MacLean, J. H. van der Waals, and E. L. Mackor, *ibid.*, **1**, 247 (1958).

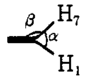
(17) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970); **94**, 2034 (1972).

(18) N. C. Baenziger and A. D. Nelson, *ibid.*, **90**, 6602 (1968).

(19) Owing to considerable interdependency among the variables in this problem and the large size of the system, it has not been possible to optimize this structure to our usual degree of refinement (*i.e.*, 0.01 Å on bond lengths and 1° on bond angles). The geometry we quote is believed to be optimum to at least 0.02 Å and 2° for lengths and angles, respectively, and the total energy to better than 0.001 au.



IV



V

bons C_2–C_3–C_4–C_5 and hydrogens H_2, H_3, H_4, H_5) to be fixed at the standard model geometry of benzene. We find

$r(C_1C_2) = 1.414$ Å $\angle C_2C_1H_1 = 121.8°$

$r(C_1C_6) = 1.451$ Å $\beta = 93.9°$

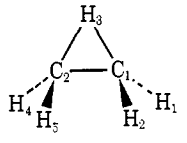
$r(C_1H_7) = 1.333$ Å $\alpha = 93.4°$

$r(C_1H_1) = 1.090$ Å

β is the angle between the carbon plane and the plane $C_1H_7C_6$; α is that between the planes $C_1H_7C_6$ and $C_1H_1H_6$.

This form (the benzenonium ion) deviates less from parent benzene than that of structure I. The carbon–carbon bond which is bridged is lengthened by 0.05 Å over benzene, and the proton rather than lying directly over this bond (*i.e.*, $\beta = 90°$) prefers to bisect approximately the angle made by the ring and the two out-of-plane hydrogens (*i.e.*, $\beta \simeq \gamma$).

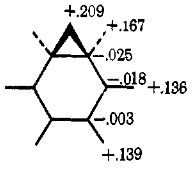
Comparison with the bridged form of the ethyl cation (VI) (see also Figure 3 of ref 7) brings to light substantial similarity in the two structures.[7] Here the proton is 1.248 Å above the CC bond (to be compared with 1.118 Å in benzenonium) and the plane made by $H_1C_1H_2$ bent 2.5° away from the line formed by C_1 and C_2, the comparable value in benzenonium being 3.4°. As previously noted, while in $C_2H_5^+$ the proton is constrained to bisect the angle made by the out-of-plane hydrogens (angle $H_1C_1H_2$), this condition, though not enforced by symmetry, is approximately met in benzenonium.



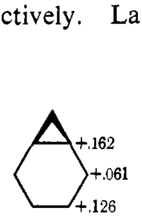
VI

We find this structure to be a saddle point on the potential surface of $C_6H_7^+$,[20] consistent with but not directly comparable with the experimental studies of Olah, Schlosberg, Kelly, and Mateescu[17] on the species in strong acid solution. A CNDO study by Jakubetz and Schuster[12] found a structure of this type to be the lowest energy form of $C_6H_7^+$. It is well established from previous work[21] that the CNDO method unduly favors bridged structures over open-chain structures, and caution should be used in its application to problems of this nature.

STO-3G total and π-electron Mulliken charges for the bridged form of protonated benzene are given as structures VIIa and VIIb, respectively. Large fluctuations such as those noted in benzenium are not to be found here, the positive charge being distributed relatively evenly over the entire molecular framework.



VIIa



VIIb

In addition to the two structures for protonated benzene already dealt with in detail, we have briefly considered two other possible forms. These are a face-protonated structure in which the proton is directly above the center of the ring and an edge-protonated form in which all atoms lie in a single plane and the entering proton is on the bisector of a carbon–carbon bond. Initial explorations on both these structures showed them to be energetically unfavorable and discouraged any further effort. Such findings are entirely consistent with published studies[22] on edge- and face-protonated forms of cyclopropane.

Table I presents theoretical total energies for benzene and the two protonated forms considered in detail in this paper. As has been our previous practice, a single calculation using the extended 4-31G basis has been performed in each case, employing the optimum STO-3G geometry (except as mentioned earlier for benzene itself where the standard model geometry is used throughout).

Table I. Theoretical Energy Data (Hartrees)

Molecule	STO-3G	4-31G
C_6H_6	−227.89006	−230.37592
$C_6H_7^+$ (I)	−228.25309	−230.67543
$C_6H_7^+$ (IV)	−228.20891	−230.64254

The theoretical proton affinities for benzene (energy of $C_6H_7^+$ (structure I) − energy of C_6H_6) are 227.8 and 187.9 kcal/mol for the STO-3G and 4-31G bases, respectively. These may be compared with an experimental value of 183 kcal/mol obtained by Haney and Franklin.[23] These results are consistent with earlier comparable studies which show that the minimal STO-3G basis substantially overestimates proton affinities while the extended 4-31G basis reproduces experimental results fairly accuately.[7,24]

It should be noted that the proton affinity of benzene is quite large, in spite of the loss of aromatic character in the benzenium ion. In fact, the value for benzene is greater than that for ethylene experimentally

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(20) In order to test that our structure II is indeed a saddle point (rather than a stable minimum), we performed a single STO-3G calculation using the optimum geometry excepting that the proton was moved 0.01 Å away from the direct center of the carbon–carbon bond. An energy lowering was found.

(21) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969).

(22) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **93**, 1813 (1971).

(23) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).

(24) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 6377 (1971).

and by both theoretical methods. This is in contrast to the prediction of the simple "localization energy" concept in Hückel π-electron theory, according to which localization of a pair of electrons in benzene involves a loss of π-electron energy of -2.536β whereas a comparable calculation on ethylene gives only -2β. Clearly other factors such as the additional σ bonds available for polarization in the larger molecule must be taken into account in discussing proton affinities.

The difference in energy between the benzenium (I) and benzenonium (IV) ions (27.7 kcal/mol for the STO-3G method and 20.6 kcal/mol using the 4-31G basis) is the barrier to proton exchange between carbon centers. Thus while structure I is a minimum on the $C_6H_7^+$ potential surface, structure IV actually corresponds to a saddle point, being unstable with respect to movement of the proton away from the exact center of the carbon–carbon bond. The corresponding barriers to proton migration in the ethyl cation have earlier been reported as 11.4 and 6.8 kcal/mol for the STO-3G and 4-31G basis sets, respectively.[7]

Conclusion

We have attempted to elucidate the structure of protonated benzene by theoretical techniques using simple *ab initio* molecular orbital theory. The general conclusions may be stated as follows.

1. We find the lowest energy structure for protonated benzene to be one in which the proton is attached directly to one of the ring carbons, which in turn has become approximately tetrahedrally coordinated. The form corresponding to the proton bridging a carbon–carbon bond is found to be 20–30 kcal/mol less stable. Edge- and face-protonated structures appear to be energetically very unfavorable.
2. The structures we report here for $C_6H_7^+$ correspond in some detail to those previously published for the ethyl cation.
3. The ptoton affinity of benzene is well described by simple molecular orbital theory (using the extended 4-31G basis) and is noted to be somewhat larger than that of ethylene. This leads to some doubt about localization energy predictions of the stabilities of compounds of this nature.
4. Using the extended 4-31G basis, the barrier to proton migration in $C_6H_7^+$ is found to be 20.6 kcal/mol, significantly larger than the corresponding quantity in the ethyl cation.

Acknowledgment. This research was supported in part by the National Science Foundation under Grant GP 25617.

Ab Initio Calculations on Large Molecules Using Molecular Fragments. Characterization of Nitrogen-Containing Molecules[1a]

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Contribution from the Department of Chemistry,
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Abstract: An *ab initio* procedure for the investigation of large molecules is applied to a series of compounds containing nitrogen as a heteroatom. In particular, the effect of the nitrogen lone pair on geometric and electronic structure predictions is studied. Several descriptions of molecular fragments are tested, in which floating spherical Gaussian orbitals (FSGO) are employed. Applications of the method to methylamine, dimethylamine, hydrazine, methylenimine, diimide, pyridine, pyrazine, and pyrrole are given. When possible, comparisons are made with other theoretical results as well as experimental values. The geometric and electronic structure predictions are, in general, very good and comparable to results obtained earlier for hydrocarbons. Those cases in which exceptions occur are discussed in detail, and suggestions are made for fragment improvements to correct the deficiencies.

In previous studies,[2–8] an *ab initio* molecular orbital method for application to large molecules has been described, and the characteristics of this method as applied to saturated and unsaturated hydrocarbons have been investigated. In this method, molecular fragments are employed to obtain the basis orbitals for use in an LCAO–MO–SCF procedure on large molecules. If this method is to be applicable in general to molecular systems for the determination of geometric structure, electronic structure, and properties, it is essential that nitrogen-containing single and double bonds also be described adequately.

This investigation emphasizes the study of the electronic and geometric structure of prototype molecules containing nitrogen as the heteroatom, in order to obtain an optimum description for future heteroatom

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(1) (a) This work was supported in part by a grant from the National Science Foundation, and a grant from the Upjohn Co., Kalamazoo, Mich.; (b) Phillips Petroleum Fellow, 1970–1971; (c) Alfred P. Sloan Research Fellow, 1971–1973.

(2) R. E. Christoffersen and G. M. Maggiora, *Chem. Phys. Lett.*, 3, 419 (1969).

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(6) R. E. Christoffersen, *Advan. Quantum Chem.*, **6**, 333 (1972).

(7) G. M. Maggiora, D. W. Genson, R. E. Christoffersen, and B. V. Cheney, *Theor. Chim. Acta*, 22, 337 (1971).

(8) B. V. Cheney and R. E. Christoffersen, *J. Chem. Phys.*, **56**, 3503 (1972).