A Theoretical Study of Benzene Protonation

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The structures of σ and π complexes of $C_6H_7^+$ are examined by both MINDO/3 and *ab initio* methods. The crucial role played by full optimization of the geometry is established. From the examination of the potential energy surface it appears that there are two different channels for benzene protonation, one through the π complex, and the other leading directly to the σ complex. The π complex may be considered to be a transition state for the intramolecular isomerization of the σ complex.

THE precise mechanism of electrophilic aromatic substitution remains a matter of discussion.[1] As a first step in a general theoretical study of this reaction we present here the results for the simplest case, the protonation of benzene. The paper is divided into two main parts: first, the structures of the σ and π complexes are reported, and secondly, the role of these complexes in the reaction mechanism is discussed in relation to detailed inspection of the potential surface.

Both the *ab initio* [2,3] and semi-empirical molecular orbital methods [4-8] have been used to study the structures of $C_6H_7^+$, the two sets of results being strikingly different. According to the *ab initio* calculations, in the σ complex the proton is bonded to a ring carbon which assumes approximately tetrahedral co-ordination, whereas in the semi-empirical calculations this carbon forms an angle of nearly 120° with the neighbouring ring atoms. We would like to underline here that while in some semi-empirical calculations [4,5] complete relaxation of the geometry has been possible, in the *ab initio* calculations the geometrical variables optimized have been drastically reduced. Thus, the divergent results may be due to the different schemes of optimization and/or to intrinsic differences in the methods of calculation. This is the first point to be examined.

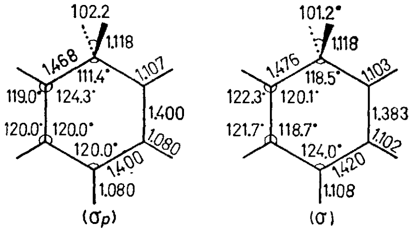
On the possible role of the π complex in the reaction mechanism several authors [3,5] have considered it as the transition state for intramolecular isomerization of the σ complex. Heidrich and Grimmer [5] have determined the energy profile for this proton shift. Later, Gleghorn and McConkey,[4] using MINDO/2′, showed that the π complex is an intermediate, not a saddle point. In all instances, the possible role of the π complex along the pathway of benzene protonation remains unanswered. This is the second point to be examined by establishing the different channels for benzene protonation through a careful examination of the potential energy surface.

METHODS

Owing to the impossibility of calculating the multi-dimensional potential energy surface for the majority of chemical reactions, two types of approximations are normally used. The first attempts to reduce the dimensionality of the surface by eliminating certain degrees of freedom. In practice, however, a sufficient reduction is impossible without imposing unrealistic conditions. The second type of approximation involves choosing one or two degrees of freedom as independent variables of the potential energy, and to allow the system to relax by optimizing all remaining parameters. This second method is a considerable improvement on the first if a careful selection of the appropriate independent variables is made. We have used this second type of approximation. Even then, the quantity of calculation makes the use of the *ab initio* method prohibitive. So, we used the MINDO/3 [9a] semi-empirical method with the Davidson–Fletcher–Powell [10] algorithm for minimization, as implemented in the program of Dewar *et al.*[9b] For the most interesting points on the energy surface *ab initio* calculations with a STO-3G basis [11] and CI have been carried out using a modified version of the GAUSSIAN 70 series of programs.[12]

RESULTS AND DISCUSSION

In order to see the influence of geometrical relaxation on the results, we carried out two series of MINDO/3 calculations for the σ and π complexes. In the first, partially optimized structures were obtained using the same restrictions as Hehre and Pople [3] (σ_p and π_p structures). In the second full relaxation of the geometry was allowed (σ and π structures).

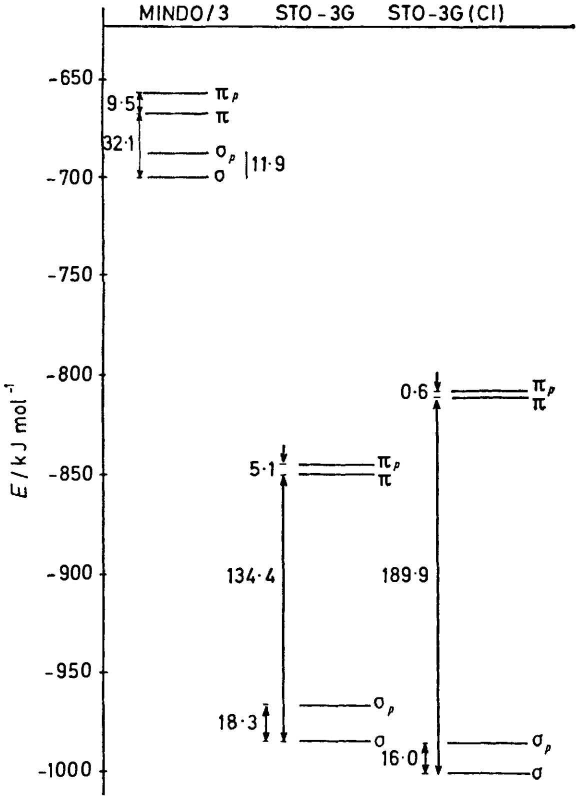


(σ_p) (σ)

FIGURE 1 MINDO/3 calculated geometry with partial (σ_p) and total (σ) relaxation

The π_p structure is very similar to that found by Hehre and Pople.[3] Full relaxation allowing a more homogeneous distortion of the ring provides a stabilization of 9.5 kJ mol^{-1}.

For the σ_p complex we imposed the ring of carbon atoms on the same plane with the standard distances [13] for the five carbon atoms C(2)—C(6) and for the three hydrogen atoms linked to C(3)—C(5). All the remaining parameters were minimized. The σ_p and σ structures obtained are shown in Figure 1. The partially relaxed structure σ_p is very similar to those obtained by *ab initio* methods.[2,3] Particularly, the C(6)–C(1)–C(2) angle has a value of 111.4° in close agreement with those of Hehre



SCHEME Energy diagram for different σ and π complexes of $C_6H_7^+$. Energy is relative to that of benzene

and Pople (110.9°)[3] and Mulliken (113.5°).[2] The fully relaxed geometry σ is 11.9 kJ mol^{-1} more stable according to the MINDO/3 method. The C(6)–C(1)–C(2) angle has greatly increased (118.5°) and we are far from tetrahedral co-ordination. From the values in Figure 1 it is clear that the tension introduced in benzene by protonation is now more homogeneously distributed over the ring.

STO-3G Calculations for σ_p, σ, π_p, and π were carried out using the geometries obtained by MINDO/3. As a further step, a limited CI was carried out. The most important orbitals in the protonation of benzene are the two pairs of degenerate orbitals in benzene and the empty one of the proton. Thus, the CI matrix was constructed with all the mono- and bi-excited configurations between these five orbitals in the complexes. The results are shown in the Scheme.

The MINDO/3 calculated proton affinity of benzene is 696.9 kJ mol^{-1}, in good agreement with the experimental values (744.8 kJ mol^{-1})[14] and (766.1 kJ mol^{-1}).[15] The STO-3G results differ greatly from the experimental data, and only when more refined basis is used[2,3] are the values satisfactory (Table 1).

The σ complex is always the most stable. The MINDO/3 value for the energy difference between the σ and π structures, 32.1 kJ mol^{-1}, seems to be in close agreement with the experimental activation energy (41.8 kJ mol^{-1})[16] for intramolecular proton exchange in $C_6H_7^+$. The STO-3G basis greatly overemphasizes this barrier, and the limited CI does not improve this result because the σ complex is more stabilized than benzene, and benzene more than the π complex. Consequently, agreement with experiment can be reached only with a more refined basis.

TABLE 1

Protonation energy (kJ mol^{-1})

Experimental	MINDO/3 *	STO-3G *	STO-3G IC *
744.8	696.9	979.7	995.3
Experimental	STO-3G †	4-31G †	Mulliken ‡
744.8	953.1	786.2	791.2

* Present work. † Ref. 3. ‡ Ref. 2 with a large contracted gaussian basis set including polarization functions.

TABLE 2

Energies (kJ mol^{-1}) for STO-3G calculations on the σ complex

Ref. 3	−599 469.9
This work (σ_p)	−599 467.2
This work (σ)	−599 485.4

Let us focus on the differences between the σ_p and σ complexes. The MINDO/3 results for σ_p are similar to the previous *ab initio* calculations.[2,3] Thus, the differences pointed out in the Introduction regarding the structure of the σ complex are a consequence of the different optimization schemes. This conclusion is reinforced by the results shown in Table 2, where the fully minimized MINDO/3 structure recalculated with STO-3G is 15.5 kJ mol^{-1} more stable than that obtained by Hehre and Pople[3] with the same basis. Consequently, if a full relaxation was made in the *ab initio* calculations, the structure obtained would be very similar to that obtained by the semi-empirical methods. It appears that the study of these complexes requires a full relaxation of the geometry. Under these conditions the classical view of the σ complex with a contraction of the delocalization (Wheland's model[17]) is not supported, it being more appropriate to speak about an extension of the delocalization according to the unified model proposed previously.[18] Experimental support for this conclusion comes from the recent paper by Olah *et al.*[19]

To study the role of the π complex in the reaction mechanism we have constructed the two energy profiles

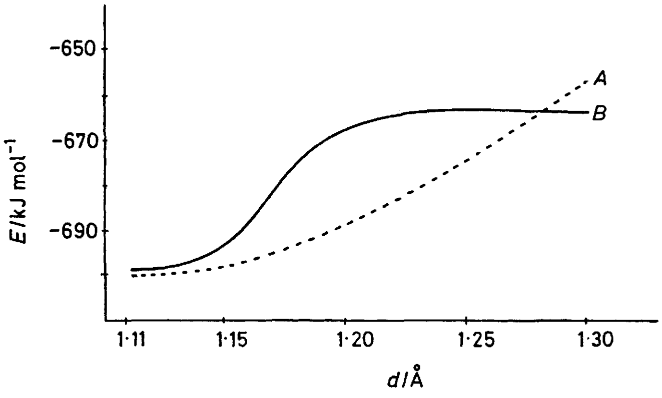


FIGURE 2 Energetic profiles for different C–H distances: A, σ complex as starting point; B, π complex as starting point

shown in Figure 2. The broken line A shows the results when starting from the σ complex; we gradually increased the C–H distance, which was taken as an independent variable minimizing all the remaining parameters. The full line B represents the transition from the π to the σ complex: starting from the π complex, the C–H distance as the independent variable was progressively shortened to 1.11 Å (the distance for the σ complex), all other degrees of freedom being minimized. The two lines cross near 1.27 Å and the π complex (C–H = 1.3 Å) is more stable than the corresponding point for the σ channel. That means that in the first stage of the reaction the π complex must play an active role. The appearance of two lines is surprising, given that the independent variable is the same and all other variables have been optimized. Thus, there must be two different channels converging to the σ complex. In order to clarify this point we present in Figure 3 two different energy surfaces constructed as follows: for a given C–H distance [1.11 Å in Figure 3(a), and 1.3 Å in Figure 3(b)] the two angles determining the position of the proton were taken as independent variables, all the remaining parameters being optimized. Only one minimum appears at 1.11 Å and so, only one channel must be present at short distances. On the other hand, at 1.3 Å there are two minima, the deeper one corresponding to the π complex and the other being located in the same region as the σ complex. The saddle point between the two minima (α 80°, β 260°) is 16.8 kJ mol^{-1} above the π complex. There are, then, two different channels, one of them leading directly to the σ complex and the other through the π complex that at shorter distances must converge to the σ complex channel. At the crossing point of the two energy profiles we calculated the energies corresponding to the two minima and the saddle point in Figure 3(b). There remains a barrier of 8.4 kJ mol^{-1} between the two isoenergetic minima providing an explanation of the fact that even at the shorter distances the two channels remain independent. When this barrier disappears the π channel flows into the σ channel.

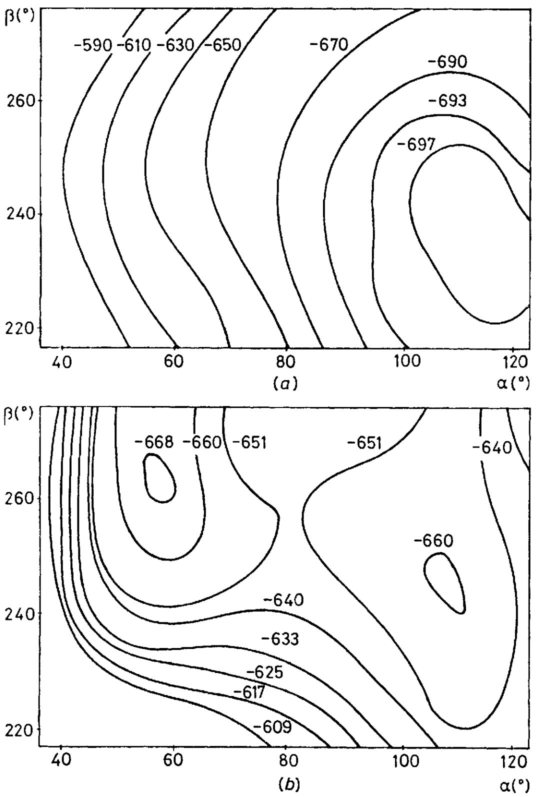


FIGURE 3 Potential surfaces for benzene protonation: α = H(7)–C(1)–C(6), β = H(7)–C(1)–C(6)–C(5), (a) C–H = 11.1 Å; (b) C–H = 1.30 Å

Our results agree with those of Heidrich and Grimmer [5] showing that the π complex may be considered a saddle point in the intramolecular proton shift, and the calculated value for the potential barrier, 32.1 kJ mol^{-1}, agree very well with the experimental activation energy (41.8 kJ mol^{-1}).[16]

Even if the finer details of the surface will ultimately be clarified by the use of extended bases *ab initio* calculations, this agreement makes us confident that the important trends of the surface would be not very different from our semi-empirical results.

In the present paper the protonation of benzene has been studied as a prototype of electrophilic aromatic substitution. Nevertheless, given that the proton is a very peculiar electrophile, since it lacks an electron, our results cannot be generalized to any other electrophilic agent without further study. This study is in progress.

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REFERENCES

[1] F. A. Carey and J. Sundberg, 'Advanced Organic Chemistry,' Plenum, New York, 1977, part A; G. A. Olah, *Accounts Chem. Res.*, 1971, **4**, 240; J. M. Ridd, *ibid.*, p. 248; G. A. Olah, M. C. Liu, J. A. Olah, and S. Naravy, *Proc. Nat. Acad. Sci. U.S.A.*, 1978, **75**, 1045.

[2] W. C. Ermler, R. S. Mulliken, and E. Clementi, *J. Amer. Chem. Soc.*, 1976, **98**, 388.

[3] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 6901.

[4] J. T. Gleghorn and F. W. McConkey, *J.C.S. Perkin II*, 1976, 1078.

[5] D. Heidrich and M. Grimmer, *Internat. J. Quantum Chem.*, 1975, **IX**, 923.

[6] W. Jakubetz and P. Schuster, *Tetrahedron*, 1971, **27**, 101; *Angew. Chem. Internat. Edn.*, 1971, **10**, 497.

[7] W. W. Schoeller and G. E. Schenck, *Tetrahedron*, 1973, **29**, 425.

[8] E. Helgstrand, *Acta Chem. Scand.*, 1970, **24**, 3687.

[9] (*a*) R. C. Bingham, M. J. S. Dewar, and D. M. Lo, *J. Amer. Chem. Soc.*, 1975, **97**, 1285; (*b*) M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. M. Lo, C. A. Ramsdem, H. Kollmar, P. Werner, and P. K. Bischot, program no. 279, Q.C.P.E., University of Indiana.

[10] W. C. Davidson, *A.E.C. Res. Develop. Rep. A.N.I.*, 1959, 5990; R. Fletcher and M. J. D. Powell, *Computer J.*, 1963, **6**, 163.

[11] W. J. Hehre, R. F. Stewar, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[12] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Q.C.P.E., University of Indiana.

[13] J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

[14] Sh. L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.*, 1972, **94**, 6630.

[15] Data quoted in footnote 16 of ref. 2.

[16] G. A. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1970, **92**, 2546.

[17] G. W. Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

[18] J. Bertrán, O. Chalvet, R. Daudel, T. F. W. McKillop, and G. H. Schmid, *Tetrahedron*, 1970, **26**, 339.

[19] G. A. Olah, J. S. Staral, G. Asencio, G. Liang, D. A. Forsyth, and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1978, **100**, 6299.