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BENZENE-H^+ AND BENZENE-Li^+ COMPLEX FORMATION - A THEORETICAL SUGGESTION OF DIFFERENT STRUCTURE

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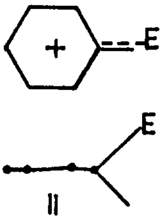
The protonation of benzene and other aromatic compounds in the gas phase has been studied theoretically in some detail. The quantum chemical calculations showed the face protonation (centrosymmetrical H^+-position) I (E = H) to be energetically unfavourable in comparison with H^+-positions near atom and bond regions of the benzene ring (σ-complex II and the bridged structure IV).[1-4] The "tetrahedral" σ-complexes II (E = H) are in general calculated as deepest minima on the potential surface of protonated arenes in qualitative agreement with experimental results in solution (cf. ref.[1]) where the influence of solvent molecules and counterions additionally exists. For aromatic compounds of low reactivity the stability of the nonclassical bridged structure IV (E = H) is calculated to be energetically near the classical σ-complex II.[5,6]

I



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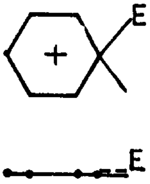

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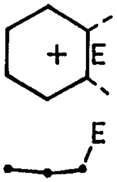

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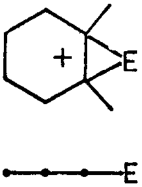

V

In comparison with protonated benzene we found a completely different stable structure of the benzene-Li^+ complex.

Computational methods: We used the CNDO/2-FK method in line with an automatic procedure for complete geometry optimization.[5,6] This semiempirical method was found to be successful in calculating structures of protonated unsaturated systems of the given type.[1,8,9] We additionally calculated the essential properties of the potential surface by CNDO/2 in the original parametrization (CNDO/2-PSS)[10]. The results of this method for protonated benzene are well-known and have been discussed critically.[1] However, both methods give the same qualitative result of a strong energy difference between face protonation on the one side and the σ- and π-complex structures on the other side in accordance with the results of ab initio methods[3].

Results and discussion: Values for the calculated energies (CNDO/2-FK) of complex structures relative to the energy of the face structure can be seen in table 1. The structure with lowest energy for benzene-Li$^+$ is the hexagonal π-complex (face form I) in contrast to the benzene-H$^+$ system, where the face structure is a high maximum on the surface. We found rearrangement without a barrier to the face form from the σ-complex II (E = Li) or the bridged structure IV (E = Li) as starting geometries for the minimization procedure. Considering the experimental value of the Li$^+$ affinity of benzene determined in the gas phase (155 kJ mol^{-1})[11] one has to assume an overestimation in the calculated values (CNDO/2-FK) relative to the face structure by a factor of about 3.*) All the mentioned properties of the Li$^+$-benzene surface are qualitatively the same using the CNDO/2-PSS method. The energy minimum for benzene-Li$^+$ is very flat. A Li-shift of 0,35 Å (CNDO/2-FK) and 0,5 Å (CNDO/2-PSS) towards a σ-complex structure yields here only an increase in energy by about 1,5 kJ mol^{-1}.

Table 1.
CNDO/2-FK energies ΔE(kJ mol^{-1}) for some characteristic points on the potential surface of the benzene-Li$^+$ and benzene-H$^+$ systems (relative to the face structure)

structure	ΔE benzene-Li$^+$	ΔE benzene-H$^+$
face (I)	0	0
σ-complex "tetrahedral"(II)	(320±20)+)	-290
planar (III)	++)	-153
bridged (IV)	++)	-262
edge (V)	321	-95

+)no stationary point ++)these unstable arrangements were not tested for saddle points and maxima.

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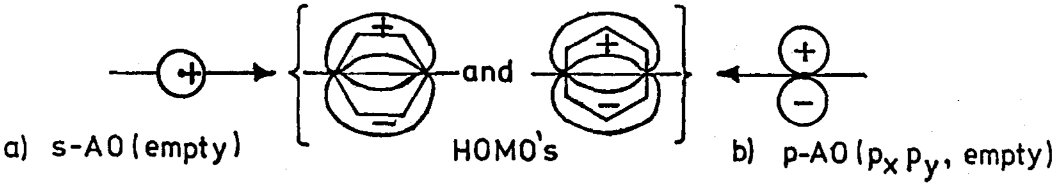
*)The face structure with π-bonding to 6 equivalent centres is a special case for overestimation of the stability of "bridged" arrangements by semiempirical methods.

Our calculations show the planar structure V (III rearranges to V in the molecular plane) of the benzene-Li^+ system energetically comparable with a σ-complex structure II. Similar trends were found recently by Pople et al.[12]

First calculations (CNDO/2-PSS, sp basis) on the benzene-Na^+ system result also in a more stable face structure I ($E = Na$) relative to a "tetrahedral" one.[13,14] In contrast to the benzene-Li^+ system we find both structures to be separated by a potential barrier.

Qualitative MO interpretations in terms of symmetry may be used to explain the relative energy of the face structure. In this way the discrimination of the face protonation can be understood by the orthogonality of the unoccupied s-atomic orbital of the proton with respect to the (degenerated) highest filled π-MO's (HOMO's) of the benzene ring a).[15] However, for Li^+ low acceptor orbitals are also p-orbitals, where the degenerated pair p_x, p_y has the symmetry for bonding with the π-HOMO's of the benzene system (π-interaction b). The calculated wavefunction shows, that this interaction contributes considerably to the strong energy decrease of the face structure in the benzene-Li^+ system. If this will be confirmed by further calculations we would have to revise the idea that the interaction of metal cations (elements of the groups I, II and III in their maximum oxidation state) with benzene would be mainly characterized by the orthogonality of the free 2s or 3s atomic orbitals of the cation to the highest filled π-orbitals of the ring.



Up to now experimental studies on the formation of cation-molecule complexes in the gas phase have given only little information concerning their ground state structure. Another possibility to get such informations follows from the study of nuclear magnetic resonance spectra (nmr) of adsorbed molecules on different cation forms of zeolites.[16-18] The comparison of experimental ^{13}C-nmr shifts with calculated ones for certain models of surface complexes can give information concerning geometric and electronic structures of molecule-cation complexes. So a centrosymmetrical arrangement of the benzene ring over a Na^+-ion was found for arenes (benzene, toluene) in NaX- and NaY-zeolites[18,19] in agreement with the theoretical suggestions. These results have been confirmed additionally by ^1H-nmr measurements at low temperature (77 K).[2o] The stronger interaction of Li^+ with benzene should result in a dominant Li^+-benzene interaction in Li^+ exchanged zeolites and a corresponding centrosymmetrical arrangement of the benzene molecules over Li^+ ions in these zeolites. Nmr measurements on Li^+ exchanged zeolites are in progress.

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