(180 mg, 1.00 mmol) were mixed in THF (10 mL). The mixture was stirred for 65 h at room temperature and then heated at reflux for 15 h. Purification by SiO_2 flash chromatography (22 cm, ∅2 cm, AcOEt:cyclohexane (97:3)→(20:80), 20 mL) allowed the partial separation of three diastereoisomers of the desired product as pale yellow oils: *cis*-**7** (71 mg, 30%) and *trans*-**7** (112 mg, 48%, d.r. = 92:8). Combined yield: 78%, d.r. = 56:39:5. Starting material (25 mg, 14%) was also recovered. See the Supporting Information for spectroscopic details.

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Do Isopropyl and *tert*-Butyl Cations Form π Complexes with Benzene?**

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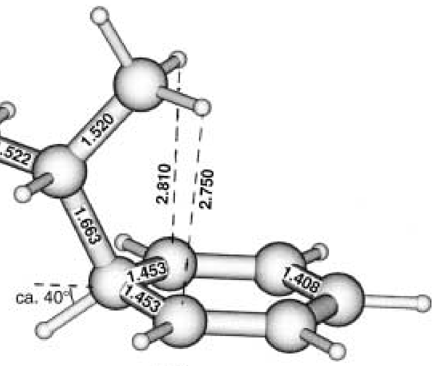
The question of formation of π complexes in electrophilic aromatic substitution (EAS) has been debated for a long time.[1–4] The answer to this question is fundamental for setting up the mechanism of EAS and, therefore, for the interpretation of the kinetic data. Quantum chemistry plays a key role in the assessment of the complex formations. Herein we deal with the identification of π complexes that may be formed from benzene and carbocations.

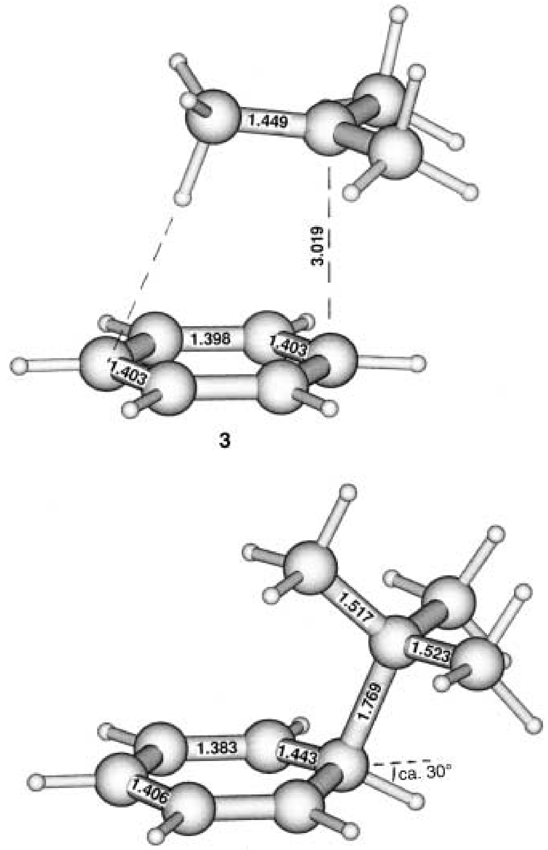
If we initially consider the structure of protonated benzene, π complexes of benzene with H^+ are not found by using the potential energy surface of the benzene–H^+ system. The only minimum is formed by the σ complex (benzenium ion).[5,6] The latter is also observed under mass spectrometric conditions[7] as well as in superacidic acids.[8] A "face" protonation is strongly disfavored.[5,6] The question arises, whether the knowledge about the protonation is qualitatively also valid for the carbocation attack on benzene.

The attack of CH_3^+ on benzene leads barrierless to a σ complex.[9] Our quantum-chemical studies on the interaction of the isopropyl cation with benzene do not give a π-complex intermediate (without the inclusion of electron correlation a conflicting result is obtained[10]). Like CH_3^+, the naked isopropyl cation approaches the benzene molecule barrierless to form the σ complex **1a** (Figure 1). In a recent theoretical paper on the alkylation of naphthalene,[11] π-complex formation was not included. We do find a π complex (**3**) for the attack of the *tert*-butyl cation ($t\mathrm{Bu}^+$) on benzene preceding the σ complex **4** (Figure 2). In contrast to the results in reference [10], the cationic electrophile is not centered above the ring centroid. The "face" structure **5a** (C_3) is, analogously to benzene–H^+, a saddle point of index 2 and is $\Delta H^{\circ}(0) = 2.5\ \mathrm{kcal\,mol^{-1}}$ higher in energy than the σ complex (≈ 7 kcal mol^{-1} with respect to ΔE_{pot}, Table 1). Another three quasi-"face" structures **5b** (C_s) are saddle points of index 1. They are $\Delta H^{\circ}(0) = 2.1\ \mathrm{kcal\,mol^{-1}}$ more unstable than the σ complex (6 kcal mol^{-1} with respect to ΔE_{pot}). The most probable position of the $t\mathrm{Bu}^+$ (definded by the position of the central C(δ$^+$)atom, $C_{t\mathrm{Bu}^+}$) is calculated to be along the ring carbon atoms and their C–C bonds. Directly over the ring carbon atoms (distance $C_{t\mathrm{Bu}^+}$–$C_{\mathrm{benzene}} = 3.02$ Å) there is a



1a

Figure 1. The σ complex **1a** of the isopropyl cation with benzene (C_1 symmetry).



3

4

Figure 2. The π complex **3** (C_s) and the σ complex **4** (C_s) of the system [benzene + *tert*-butyl cation] (numbering according to Table 1; bond lengths [Å], angles [°]).

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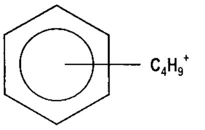
Table 1. Selected total energies E_t and relative energies ΔE_{pot} and $\Delta H^{\ominus}(0)$.[a]

Structure/Compound		Symmetry	E_t [Hartree] (index)[b]	E(ZPV) [kcal mol^{-1}]	$\Delta H^{\ominus}(0)/\Delta E_{pot}$ [kcal mol^{-1}]	
benzene		C_{6h}	−231.519173 (0)	62.7	PA[c]	174.6/181.9
propene		C_s	−117.510856 (0)	51.1	PA	176.5/182.1
isobutene		C_{2v}	−156.699867 (0)	69.2	PA	192.0/196.1
isopropyl cation		C_2	−117.801025 (0)	56.7		
tert-butyl cation		C_1	−157.012347 (0)	75.0		
		C_1[d]	−157.012367 (0)	75.1		
benzene + isopropyl cation:						
σ complex[f]	**1a**	C_1	−349.372478 (0)	125.1	σ-mon[f]	−27.1/−32.8
	1b	C_s	−349.371103 (0)	125.4		
TS (σ–σ)	**2**	C_s	−349.356516 (1)	124.4	barr[f]	9.3/10.0
benzene + tert-butyl cation:						
π complex	**3**	C_s	−388.556170 (0)	139.8	π-mon[f]	−13.4/−15.5
					π-mon[g]	−9.9/−12.1
σ complex	**4**	C_s	−388.561898 (0)	142.9	σ-mon[f]	−13.9/−19.1
					π-σ	0.6/3.6
face structure	**5a**	C_3	−388.550995 (2)	138.6	face-σ	2.5/6.8
quasi-face[h]	**5b**	C_s	−388.552265 (1)	139.0		
TS (π-σ)	**6**	C_1	−388.554350 (1)	140.4	barr (π-σ)[f]	1.7/1.1
					barr (σ-π)	2.2/4.7
TS (π-π)[i]	**7**	C_s	−388.555902 (1)	139.8	barr (π-π)	0.2/0.2

[a] $\Delta H^{\ominus}(0)$ includes zero-point vibrational energies E_{ZPV} with MP2/6–31 + G**(fc);[12] the method is found to be sufficiently reliable for calculations in carbocation chemistry.[11]. [b] Index of the stationary point (number of negative eigenvalues of the force constant matrix). [c] Proton affinities. [d] Pyramidal *t*Bu group. [e] **1a**: Figure 1; **1b**: both CH_3 groups of the isopropyl group point symmetrically away from the ring. [f] $\Delta H^{\ominus}(0)/\Delta E_{pot}$ values are given by shorthand notation of the energy differences, for example face-σ means: E(face structure)−E(σ-complex); barr: barrier, mon: monomer, etc. [g] BSSE corrected. [h] In addition to the face structure **5a** (C_3), there are further so-called quasi-face structures (C_s, **5b**) which are also no minima. In **5b** C_{tBu^+} is shifted from the ring center towards a C–C bond of the ring by about 0.3 Å. [i] The energy of the π–π transition structure (TS) is nearly identical with that of **3**; the barrier is neglegible (0.2 kcal mol^{-1}, $\nu_i = 23i$ cm^{-1}). Between two σ complexes there is no direct TS; *t*Bu$^+$ follows the MEW over the TS(σ–π) into the π-complex orbit and can reach any σ-complex from there by passing the TS(π–σ).

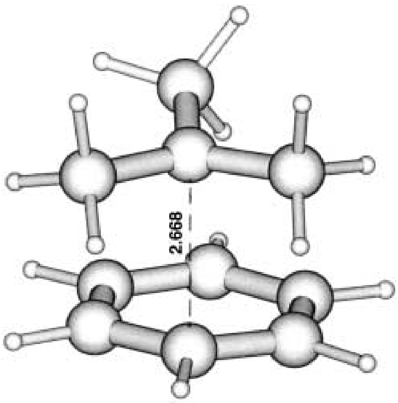
negligible higher stability of −0.2 kcal mol^{-1} (Table 1) compared with arrangements of C_{tBu^+} over benzene C–C bonds (distance 3.10 Å). In other words, the center of *t*Bu$^+$ is not fixed along the π-electron belt around the benzene ring. Hence, the present π complex is well represented by the description frequently used for putative or real π complexes of cations with benzene (cf. ref. [1]).



The formula demonstrates the great mobility of the *t*Bu$^+$ group along the benzene periphery (the formula cannot be used in the same sense for H$^+$ which does not form a π complex with benzene). The "π-complexation" energy with the *t*Bu$^+$ group is $\Delta H^{\ominus}(0) = -13.4 (\Delta E_{pot} = -15.5)$ kcal mol^{-1} and is corrected for the basis set superposition error to give −10 (−12) kcal mol^{-1} (Table 1). The *t*Bu$^+$ subunit remains nearly planar, the positive charge is still located at this group, which explains the isomerizations of the alkyl side chain.[14]

π-Complex formation proceeds as follows: If C_{tBu^+}, with a charge of approximately +0.5 (Mulliken population analysis), approaches the π-electron belt of benzene up to about 3 Å, the system gains energy which is essentially electrostatic in nature (ion–molecule interaction!). Here, the polarization of the π-electron cloud plays an important role. However, the bonding is further enforced and stabilized at the given distance by the formation of a single hydrogen bond (2.35 Å) between one of the (positive) H atoms of the *t*Bu$^+$ CH_3 groups and the π-overlap region (cf. Figure 1). This single hydrogen bond may be lost by rotation of the corresponding CH_3 group (Figure 3) and now C_{tBu^+} is able to further approach the benzene carbon atom by forming the σ complex (C_{tBu^+}–$C_{benzene}$ distance: 1.77 Å). However, the energy gain is limited due to the increasing steric hindrance and the increasing zero-point vibrational energy.

Importantly, the formation of the σ complex gives, in comparison to the π complex, a similar binding energy and therefore, a sufficient equalization of the stability of both complexes (despite of the very different distances between the



6

Figure 3. Benzene + *tert*-butyl cation: Transition structure **6** (C_1) between π and σ complexes viewed from the right on **3** (Figure 2) to indicate the rotation of CH_3 group at the back.

subunits of the complexes). As expected, σ complexation with the isopropyl cation shows much larger binding energy, $\Delta H^{\circ}(0) = -27.1$ and $\Delta E_{\text{pot}} = -32.8$ kcal mol^{-1} (Table 1). Here, the π complex disappears in the steep energy descent towards the σ complex. In electron-deficient arenes the probability of π-complex formation could be increased for the isopropyl cation.[14b] The transition structure (Figure 3) between the π and σ complex of the $[C_4H_9–C_6H_6]^+$ system occurs at $R(C_{t\text{Bu}^+}–C_{\text{benzene}}) = 2.68$ Å with $\Delta H^{\neq}(0) = 1.7$ and $\Delta E_{\text{pot}} = 1.1$ kcal mol^{-1}, respectively. In the opposite direction, the barrier is somewhat larger: 2.2(4.7) kcal mol^{-1}. The results indicate a short-lived π-complex intermediate. The $t\text{Bu}^+$ shifts from one *ipso*-σ-complex to the next require the intermediate change of $t\text{Bu}^+$ back into the π-complex region. From there, each of the six σ complexes can be reached by passing the π–σ barrier. Figure 4 illustrates the energy profile.

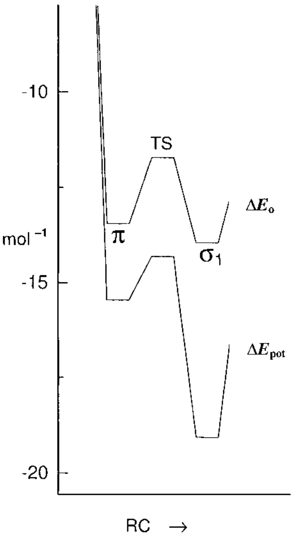


Figure 4. Energy profile of the gas-phase reaction of benzene with $C_4H_9^+$ starting from the π complex formation and the subsequent transition structure to the σ complex; $E(\text{benzene} + t\text{Bu}^+) = \text{zero}$. The upper curve represents the zero-point energies (good approximation to the relative enthalpies); the potential energies below are shown for comparison.

Summarizing the results, we find an early π-complex during the attack of the *tert*-butyl cation on benzene which shows a high extent of nonrigidity along the ring periphery of benzene. The interactions are realized by electrostatic forces and a single hydrogen bond which keeps $t\text{Bu}^+$ at a distanceof 3 Å to the benzene ring. The barrier for the $t\text{Bu}^+$ transition from the π complex to the σ complex essentially results from the loss of the hydrogen bond between the reactants by rotation of the H donor, the CH_3 group of the $t\text{Bu}^+$.

Our results show a remarkable relation with those of gas-phase electrophilic aromatic substitution of alkyl cations with arenes studied by mass spectrometric[14–16] and radiolytic techniques.[17] Holman and Gross showed that σ and π complexes coexist as interconvertible species where the existence of π complexes is unambiguous for the interaction with large carbocations such as butyl and pentyl cations.[14a] The considerable π-complex stabilization of carbocations (here about 10 kcal mol^{-1}) at a large distance from the benzene ring has also importance for the formation of carbocation intermediates in enzymatic reactions.[9] It remains to note that the existence of π complexes in condensed-phase electrophilic aromatic substitution cannot be determined unabiguously based on results of gas-phase ion chemistry. However, the extensive indirect evidence found by Olah[2] provides a strong indication for the existence of π complexes also in solution, that is we can suppose that there is frequently a qualitative similarity between the structure formation in ion–molecule reactions (gas) and the corresponding electrophilic attack in certain solutions.

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