Changes of the Aromatic Character of the Ring in Exocyclically Substituted Derivatives of Benzylic Cation as a Result of Varying Charge at the *exo*-Carbon Atom

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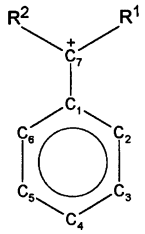
Analysis of the molecular geometry of the ring in 18 exocyclically substituted benzylic cation derivatives shows that an increase of delocalization of the positive charge over the ring is associated with a considerable decrease of its aromatic character. Separation of the aromatic character into energetic and geometric terms allows one to conclude that the effect of dearomatization due to delocalization of the positive charge in the ring is mostly reflected in the geometric term, i.e. by an increase of the alternation of bond lengths in the ring.

Benzylic cation and its substituted derivatives are very important models, since they simulate transition states in solvolysis of α-cumyl-like systems. Such systems were originally chosen as standards for the reaction series which determine the σ^+ substituent constants.[1,2] These constants are particularly important for describing the substituent effects on chemical reactivity and on physicochemical properties of the systems in which positively charged "reaction sites" are in cooperative interactions with electron-donating substituents. The most effective way of accounting for this kind of interaction is the Yukawa–Tsuno equation,[3,4] in which the σ^+ constants play a fundamental role as the reference parameters for through-resonance interactions:

$$\delta Q = \rho[\sigma^\circ + r(\sigma^+ - \sigma^\circ)], \quad (1)$$

where δQ stands for the property taken into account, σ^0 is the normal substituent constant which does not involve any additional π electron interaction between the para substituents and the reaction center, ρ is the usual Hammett reaction constant and r is the coefficient describing the size of the cooperative interactions between the substituents and the reaction sites. A recent communication[5] showed that the resonance demand expressed by the r-value is related to the relative stability of the cation and the net charge at the exocyclic carbon atom, q(C7), being associated with the value of torsion angles R1C7C1C2, θ (Scheme 1).

The aim of this report is to look at these problems from the other side. Namely how the changes of charge at the exocyclic carbon atom manifest in geometry (bond lengths) of the ring, which, in turn, may be used to define the aromatic character of the ring as studied by use of aromaticity indices BAC[6,7] or HOMA[8,9] or by use of the HOSE model[10] to estimate the weights of canonical structures describing changes of π electron structure in the ring. This kind of analysis may also shed light on the role of extra charge from the exocyclic substituent on the geometry and in consequence on the aromatic character of the ring in question.



Scheme 1.

Results and Discussion

First of all, the geometry of the ring (i.e. CC-bond lengths and bond angle at the ipso carbon atom) varies considerably with changes of the charge at C7. These changes are a direct consequence of respective change of substituents at the exocyclic carbon atom. In a series of eighteen 7-monosubstituted and 7,7-disubstituted derivatives of benzyl cation, the range of C1C2 or C1C6 bond lengths variation is as large as 0.09 Å, whereas the C2C1C6 bond angle changes in the range of 3°, the other geometric parameters being less but still significantly varied (Table 1). A characteristic feature of these changes is that, with an increase of a positive charge at C7, the alternation of bond lengths in the ring becomes less pronounced. This effect may be studied by use of the HOSE model[10] (abbreviation of Harmonic Oscillator Stabilization Energy) which allows one to estimate the weights of canonical structures from bond lengths of a given π electron

Table 1. Structural Parameters (Taken from Ref. 13) and Indices of Aromaticity for Compounds Analyzed in the Paper

Substituents of the benzylic cation	C1–C6	C1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C1–C7	q(C7)	HOMA	EN	GEO	BAC
7-CF_3	1.445	1.443	1.360	1.403	1.406	1.359	1.353	−0.222	0.721	0.000	0.279	0.520
7-CF_3-7-Me	1.440	1.438	1.362	1.400	1.398	1.364	1.379	0.000	0.712	0.039	0.249	0.588
Unsubstituted	1.436	1.437	1.362	1.403	1.403	1.362	1.357	−0.247	0.725	0.041	0.234	0.589
Me	1.429	1.428	1.368	1.396	1.402	1.364	1.378	−0.019	0.806	0.025	0.169	0.653
t-But	1.427	1.429	1.364	1.402	1.393	1.370	1.386	−0.008	0.815	0.023	0.162	0.663
o-Me-7-*t*-But	1.446	1.435	1.359	1.402	1.389	1.379	1.380	−0.025	0.711	0.048	0.240	0.612
o,*o*′-Di-Me-7-*t*-But	1.458	1.450	1.371	1.392	1.389	1.373	1.383	−0.011	0.605	0.078	0.317	0.589
7,7-Di-Me	1.424	1.423	1.369	1.395	1.395	1.369	1.404	0.195	0.859	0.015	0.127	0.707
7-Et,7-Me	1.422	1.422	0.370	1.394	1.394	1.370	1.407	0.207	0.870	0.014	0.117	0.720
7,7-Di-Et	1.422	1.422	1.371	1.394	1.394	1.371	1.410	0.217	0.874	0.015	0.111	0.727
7,7-Di-iso-Prop[a)]	1.424	1.423	1.371	1.393	1.392	1.371	1.418	0.240	0.868	0.013	0.119	0.723
7,7-Di-iso-Prop[a)]	1.419	1.419	1.372	1.392	1.392	1.372	1.419	0.239	0.895	0.010	0.095	0.751
7,7-Di-iso-Prop[a)]	1.422	1.422	1.372	1.392	1.392	1.372	1.425	0.266	0.877	0.014	0.109	0.737
7-Me-7-iso-Prop[a)]	1.423	1.422	1.372	1.392	1.394	1.369	1.412	0.228	0.868	0.015	0.117	0.721
7-Me-7-iso-Prop[a)]	1.423	1.422	1.370	1.394	1.393	1.371	1.410	0.211	0.868	0.015	0.117	0.721
7-Me-7-*t*-But	1.419	1.420	1.373	1.390	1.393	1.371	1.423	0.247	0.891	0.010	0.098	0.748
7-Iso-Prop-7-*t*-But	1.414	1.414	1.374	1.390	1.390	1.375	1.434	0.276	0.925	0.005	0.070	0.790
7,7-Di-*t*-But	1.394	1.394	1.383	1.386	1.386	1.383	1.482	0.316	0.995	0.000	0.005	0.947

a) Various conformations of the isopropyl groups.

system. The contribution of the i-th resonance structure C_i in a description of the real molecule is inversely proportional to its destabilization energy, i.e. the energy by which the i-th structure is less stable than the real molecule:

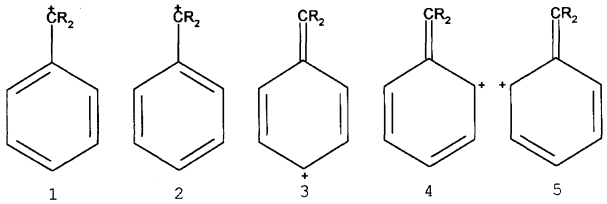
$$C_i = \frac{(\mathrm{HOSE}_i)^{-1}}{\sum_{j=1}^{N}(\mathrm{HOSE}_j)^{-1}}, \qquad (2)$$

where N is the number of resonance structures taken into consideration. The HOSE term is calculated following the formula:

$$\mathrm{HOSE}_i = -E_{\mathrm{def}} = 301.15\left[\sum_{r=1}^{n_1}(R_r' - R_0^{\mathrm{s}})^2 k_r + \sum_{r=1}^{n_2}(R_r'' - R_0^{\mathrm{d}})^2 k_r\right], \qquad (3)$$

where R_r' and R_r'' stand for the lengths of π bonds in the real molecule, whereas n_1 and n_2 are the numbers of corresponding formal single and double bonds in the i-th resonance structures, respectively. In the process of virtual deformation, the n_1 bonds (which correspond to single bonds in the i-th resonance structure) are lengthened, whereas the n_2 bonds (which correspond to double bonds) are shortened to the lengths R_0^{s} and R_0^{d}, respectively, i.e. to the single and the double bond lengths in butadiene-1,3. Linear dependence between bond lengths R_r and force constants k_r is assumed. For details on the HOSE model see reference 10 or 11, or the review.[12] The model may be used for any bond lengths precisely determined by either experimental or theoretical techniques. Scheme 2 presents most important canonical structures for the skeleton of benzylic cation.

The HOSE model is applied to the ab initio (RHF/6-31G*) geometry of the ring of 18 7-mono- and 7,7-disubstituted derivatives of benzylic cation.[5,13] Then the changes in weights of canonical structure may be compared with the changes of charge at C7. In fact, they are related in a regular



Scheme 2.

way; the greater the positive charge at C7 is, the lower the weights of the quinonoid-type canonical structures (**3**—**5** of Scheme 2) which are observed. The correlation coefficient for the strongest dependence, weight of **3** vs. q(C7), is 0.727, which is equivalent to the significance level α=0.0006%.[14] Undoubtedly, the localization of the positive charge at C7 favors equalization of bond length in the ring, and is associated with larger weights of **1** and **2**, whereas its delocalization is associated with a shortening of C1C7 bond and with an increase of weights of canonical structures **3**—**5** most effectively expressed for **3**.

In order to relate these effects quantitatively to the aromatic character of the ring we have applied two indices of aromaticity based on bond lengths. The first index is called BAC (Bond Alternation Coefficient)[8] and measures directly the degree of bond length alternation:

$$\mathrm{BAC} = 1 - 3.46\sqrt{\sum_r (d_r - d_{r+1})^2}, \qquad (4)$$

where the summation runs over all differences of the consecutive pairs of bond lengths, d_r and d_{r+1}. BAC is equal to 1.0 for a ring in which all bonds are of equal lengths, and to 0.0 for rings in which bond lengths are as in the reference nonaromatic system –butadiene-1,3 with bond lengths C–C and C=C equal to 1.467 and 1.349 Å, respectively.[15] This index does not take into account an important fact that there may be no alternation also in systems with relatively long

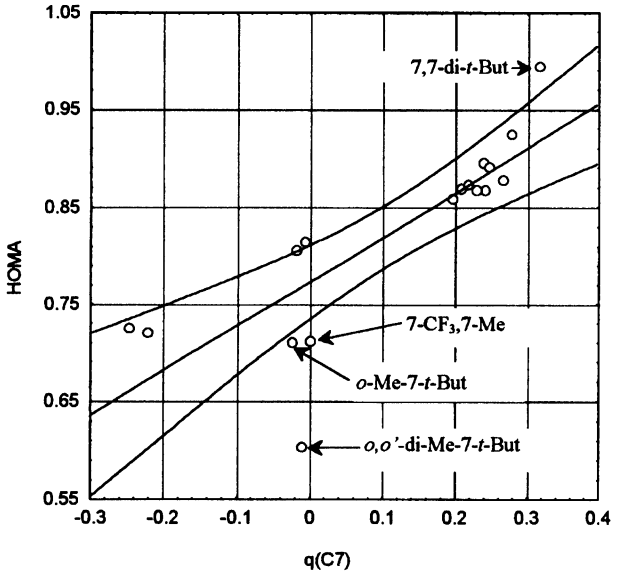


Fig. 1. The HOMA values plotted against q(C7). Correlation coefficient r=0.88, significance level α=0.0038%.

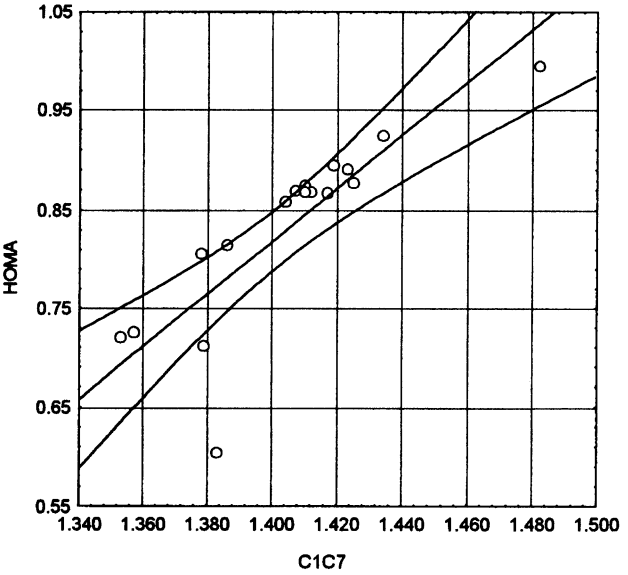


Fig. 2. The HOMA values plotted against R(C1–C7). Correlation coefficient r=0.845, significance level α=0.0010%.

bonds, and therefore with no or very little aromatic character. This shortcoming is removed in another aromaticity index based on bond length, i.e. HOMA (Harmonic Oscillator Model of Aromaticity)[8,9] which describes the variation of bond lengths in reference to what is called the optimal bond length, d_{opt}, (1.388 Å for CC bonds), i.e. the CC bond length for a situation in which single and double CC bonds are energetically averaged with the use of the harmonic potential for expansion of double bonds and compression of single bonds.[8] The HOMA index reads:

$$\mathrm{HOMA} = 1 - \frac{257.7}{n}\sum_i (R_{opt} - R_i)^2, \qquad (5)$$

where 257.7 is a coefficient which gives HOMA=1.0 for the systems with all CC-bond lengths equal to the reference length i.e. 1.388 Å and HOMA=0.0 for CC bonds with lengths as in butadiene-1,3.[15]

The HOMA index may be used for the total molecules or for their fragments, i.e. to detect local aromaticity. It has been successfully used in describing the aromatic character of many, very different π systems: Among others, nonplanar benzene rings in metacyclophanes[8] and in the folded octa-substituted derivatives of naphthalene,[8] in benzene rings embedded in various topological environments[6–8] of benzenoid hydrocarbons and of fullerenes,[16] to benzene rings in the charged systems (charge transfer complexes)[7] or in para-disubstituted benzene derivatives[17] and also in nonalternant systems like derivatives of fulvene and heptafulvene,[18] and even in the case of complexes of cyclopentadiene with metals and half metals.[19] Therefore we have decided to use the HOMA index in analyzing the relation between the changes in charge at C7 and the aromatic character of the ring in the title compounds.

According to recent papers by Katritzky et al.,[20–23] Jug and Koester[24] and our own studies,[6,17] aromaticity is a multidimensional phenomenon. It is also worth mentioning that the two above mentioned indices differ in that BAC is a typically geometric index (it measures directly and only the bond alternation), whereas HOMA measures additionally the difference between the mean bond length of the system under study and the reference bond length d_{opt}=1.388 Å. Thus it also contains some contribution from the energetic part of the aromaticity, since the mean bond lengths correlate with bond energies.[25] Very recently, an analytical way of separation of the geometric and energetic contributions to the values of index HOMA has been shown[25]

$$\frac{\alpha}{n}\sum_i (R_{opt} - R_i)^2 = \alpha(R_{opt} - R_{av})^2 + \frac{\alpha}{n}\sum_i (R_{av} - R_i)^2, \qquad (6)$$

which may be rewritten as

$$\mathrm{HOMA} = 1 - \mathrm{EN} - \mathrm{GEO}, \qquad (7)$$

where

$$\mathrm{GEO} = \frac{\alpha}{n}\sum_i (R_{av} - R_i)^2, \qquad (8)$$

$$\mathrm{EN} = \alpha(R_{opt} - R_{av})^2, \quad \text{for } R_{av} > R_{opt}, \qquad (9a)$$

and

$$\mathrm{EN} = -\alpha(R_{opt} - R_{av})^2, \quad \text{for } R_{av} < R_{opt}. \qquad (9b)$$

The interpretation of these two terms is as follows: The GEO term measures directly the degree of alternation of bond lengths in question since, in principle, this terms is a function of variance, whereas the EN term measures the loss of stability, which traditionally is related to the resonance energy. Thus an increase of GEO means an increase of bond length alternation, whereas an increase of EN means a decrease of resonance energy. Note that EN and GEO terms are subtracted from unity in the equation for HOMA (7); thus they are measures of the DEAROMATIZATION due to energetic and geometric reasons respectively.

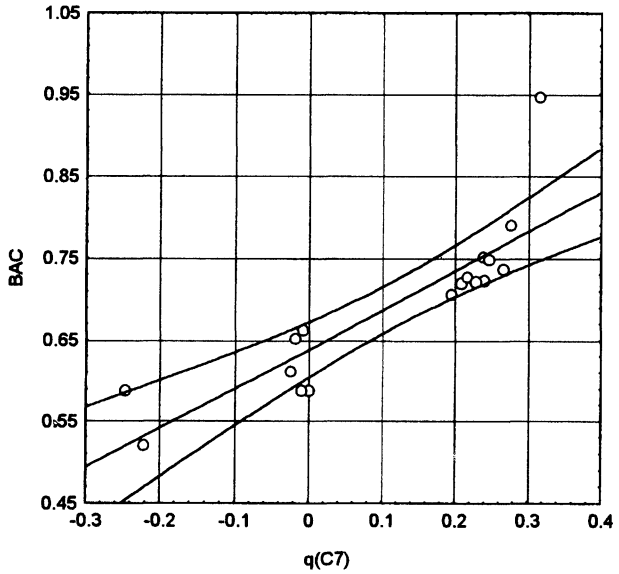


Fig. 3. The BAC-values plotted against q(C7). Correlation coefficient r=0.864, significance level α=0.00038%.

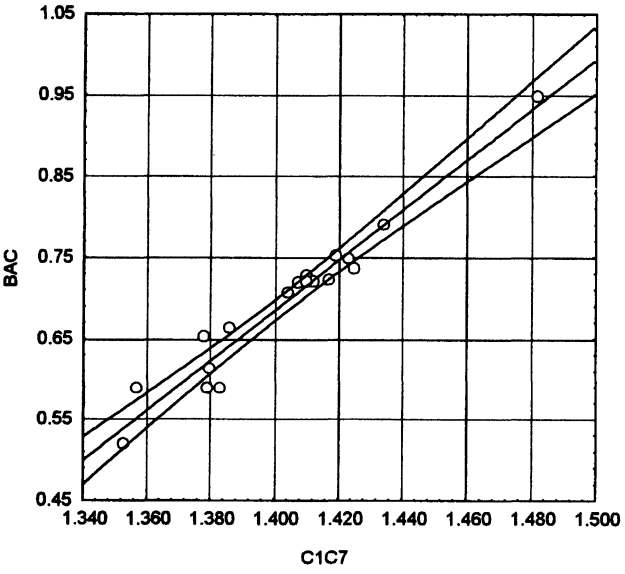


Fig. 4. The BAC-values plotted against R(C1–C7). Correlation coefficient $r=0.974$, significance level $\alpha=$ 0.000000008%.

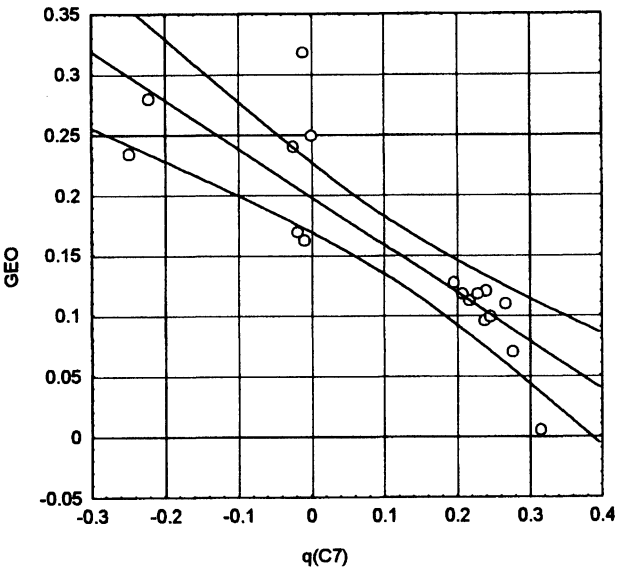


Fig. 5. The GEO-values plotted against q(C7). Correlation coefficient r=0.858, significance level α=0.00052%.

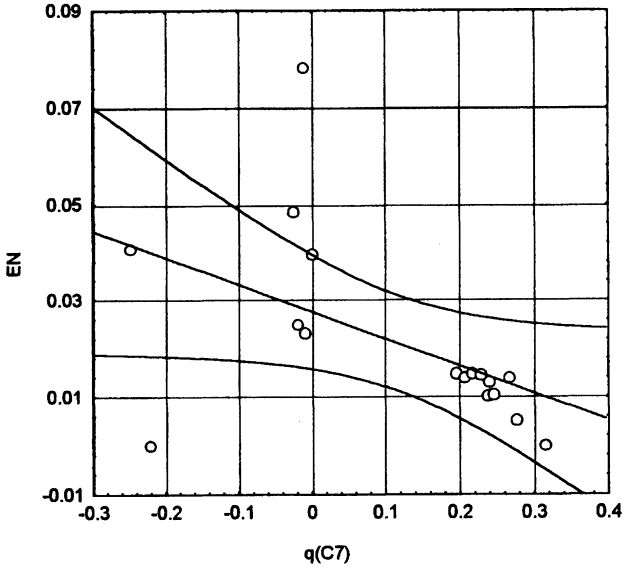


Fig. 6. The EN-values plotted against q(C7). Correlation coefficient r=0.498, significance level α=3.54%.

Now the above mentioned two terms of the HOMA index are applied to determine the degree in which the aromatic character of the ring is related to changes of the charge at C7 and of bond length C1C7 and then to show which of these two contributions plays a more decisive role in variation of the aromatic character due to change of charge at C7.

It has already been found that there exists a dependence of C1C7 bond lengths on the net charge[13] at the exocyclic carbon atom, q(C7). An increase of the positive charge at C7 is associated with the lengthening of the C1C7 bond. These two variables are statistically independent and the data points give a relatively good, monotonically curved, scatter plot. The chemical interpretation of this event is quite clear. Due to the twist around the bond C1C7 (C2C1C7R torsion angle θ), the positive charge at C7 becomes more localized, since the resonance interactions of electrons at C7 with the ring are hindered. In consequence, the C1C7 bond becomes longer and the increasing weights of the canonical structures **1** and **2** of Scheme 2 are observed.

The mechanism mentioned above can also be associated with the changes in delocalization of π electrons in the ring, i.e. variation of the aromatic character of the ring should be observed. Indeed, if the aromaticity indices BAC and HOMA are plotted against q(C7) and R(C1C7), roughly linear dependences are found, which are significant at $\alpha <$ 0.001% or better. Figures 1, 2, 3, and 4 present these scatter plots. In all figures are drawn the least-squares lines and intervals of significance (95%).

In all figures, including Figs. 5 and 6, a few points deviate considerably. Two of them are *o*-Me substituted and *o*,*o*′-di-Me substituted derivatives of α-butylbenzylic cation, in which the steric factors from ortho position may be the reason of such deviations. The other point is for CF_3-substituted benzylic cation, in which the sterically regulated dependence of charge on the twist around C1C7 bond is additionally perturbed by another interaction, the strong electron attractive force by the substituent CF_3. The deviation is in direction of an increase of the positive charge at C7–in line with the electron attractive power of this substituent. In a few cases, the point for di-*t*-butyl derivative deviates. This deviation is in a direction of the decrease of positive charge at C7. This may be interpreted as a result of a strong hyperconjugative power of two *t*-butyl groups.

Now by applying two terms of Eq. 7, i.e. the GEO- and EN-terms, in regression on q(C7), we may find the answer to the question which of these two terms is more decisive in determining the changes of aromatic character due to the varying charge at exocyclic carbon atom q(C7). Figures 5 and 6 show these two regressions: For the plot of GEO vs. q(C7) the correlation coefficient is 0.86, as compared with the value for EN vs. q(C7) equal to 0.50. The first of these two regressions is significant at α=0.005%, as compared with α=3.5% for the other regression. Undoubtedly, the geometric contribution to the variation of aromatic character of the ring is much more important. When we look at the range of variation of these two terms, the range for GEO is about 4—5 times greater than that for EN. Thus not only does the GEO term correlate better with the charge variation at C7 than the EN term does, but also the range of variation for GEO is substantially larger. This means that there is a much stronger influence of the geometric term (than of the energetic one) on dearomatization of the ring due to delocalization of positive charge from C7 onto the ring.

As a final conclusion, it may be said that the changes in charge at C7 are associated with the changes in geometry in the ring and consequently with the changes of the aromatic character of the ring.

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