Magnetic analysis (NICS) of monoarylic cations. Linear relationship between aromaticity and Hammett constants (σ_p^+)

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Abstract—Density Functional Theory (DFT) calculations show that there is a linear correlation between NICS values (aromaticity criterion) and experimental Hammett (Brown) constants (σ_p^+), together with other computed parameters for *p*-substituted benzyl cations. © 2001 Elsevier Science Ltd. All rights reserved.

The Hammett constant (σ^+) is a well-established parameter that takes into account the contribution of through conjugation of substituents to electron-deficient reactivity sites attached to a benzene ring.[1] Thus, the benzyl cation has geometric parameters which show quinoid-like ring character as well as significant double bond character in the exocyclic C–C bond (due to Lewis structures b and c in Scheme 1A).[2] π-Electron-donating and -withdrawing groups at the *p*-position, respectively, stabilize and destabilize this cation (Scheme 1B), and are associated with negative and positive values of σ_p^+. Similarly a π-electron-donating substituent reduces the electron deficiency of the exocyclic carbon atom and increases both the exocyclic double bond character and the quinone-like character (Scheme 1B, (c′)–(d′)). This implies increased electron delocalization between the ring framework and the exocyclic carbon, thereby reducing the degree of aromaticity compared to that in the parent benzyl cation.[3] Similarly an electron-withdrawing substituent would be expected to lead to a corresponding increase in aromaticity.

In recent years there has been considerable interest in theoretical studies designed to lead to a greater understanding of the origin of aromaticity.[4] The nucleus independent chemical shift (NICS) criterion proposed by Schleyer et al. as a measure of aromaticity has proven extremely valuable.[5] We here report calculations of the aromaticity of 22 *para*-substituted benzylic

cations using the NICS value at the (3, +1) ring point of electron density as defined by Bader.[6] For benzene itself this point is the geometrical center of the ring, but for substituted benzenes will be slightly displaced.[7] We employ the gauge independent atomic orbital (GIAO) approach with a 6-311+G* basis set and a B3LYP density functional (GIAO-B3LYP/6-311+G*//B3LYP/6-31G*).[8] In addition to the NICS values, we report (Table 1) the calculated charge on the exocyclic carbon atom, exocyclic bond order, LUMO energy, resonance stabilization energy (RSE)[9] and also the Bird aromaticity index.[10] For charged substituents at the *p*-position, a counterion was included, since it has been shown NICS values are sensitive to the presence of such an ion.[11]
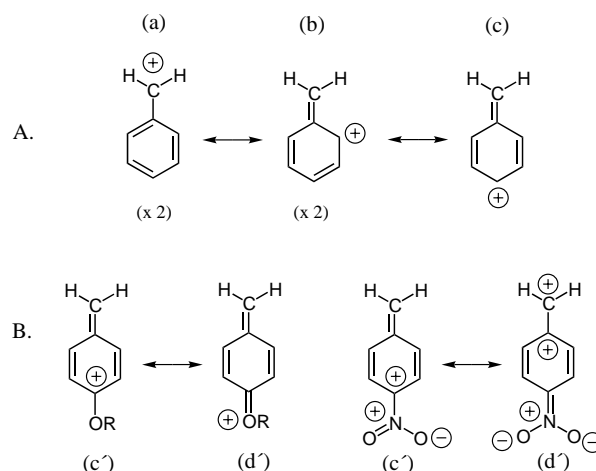
Scheme 1. Resonance structures for the benzyl cation (A) and additional canonical forms (B) when the benzyl cation has a π-*para*-substituent.

Table 1. Hammett constants $\sigma_p(+)$,[a] NICS values (ppm),[b,c] RSEs (kcal/mol),[d,e] NBO bond orders and charges,[d] LUMO energies (au)[d] and I_6[d,f] for the considered aryl cations

R	$\sigma_p(+)$[a]	NICS[b]	NICS[b,c]	RES[e]	BO_{exo}	$q(C_{exo})$	E_{LUMO}	I_6[f]
H	0.00	−1.15	−7.77	0.0	1.577	+0.45	−0.325	76
OH	−0.92	−1.19	−8.85	13.3	1.622	+0.38	−0.299	69
OMe	−0.78	−0.81	−8.75	17.2	1.629	+0.36	−0.289	67
OCOMe	0.18	−1.21	−9.06	9.5	1.615	+0.38	−0.297	70
O$^-$	−4.27	+3.80	−4.29	151.3	1.728	+0.13	−0.092	50
ONa	−2.30	+1.77	−7.14	57.2	1.682	+0.26	−0.227	58
S$^-$	−2.62	+4.30	−4.64	134.7	1.688	+0.13	−0.114	54
SNa	–	+1.59	−5.75	37.8	1.646	+0.27	−0.246	64
NH$_2$	−1.30	−0.24	−7.78	27.0	1.649	+0.33	−0.275	64
NMe$_2$	−1.70	−0.26	−7.97	33.0	1.654	+0.31	−0.261	62
NHCOMe	−0.60	−0.87	−8.52	17.4	1.629	+0.35	−0.284	67
NMe$_3^+$	0.41	−3.92	−9.23	−85.2	1.492	+0.56	−0.456	84
NMe$_3$Cl	–	−1.60	−9.10	−9.6	1.509	+0.36	−0.318	81
N$_2^+$	1.88	−5.74	−7.80	−121.3	1.413	+0.65	−0.521	97
N$_2$Cl	–	−2.33	−7.88	−12.3	1.582	+0.41	−0.324	80
NO$_2$	0.79	−3.10	−8.50	−17.5	1.549	+0.48	−0.350	78
Me	−0.31	−0.79	−7.92	7.2	1.597	+0.41	−0.310	73
CHO	0.73	−1.88	−7.32	−9.1	1.564	+0.45	−0.337	76
COOH	0.42	−1.89	−7.59	−6.4	1.566	+0.45	−0.331	77
COO$^-$	−0.41	+0.31	−7.79	99.7	1.647	+0.21	−0.155	67
COONa	−0.02	−1.10	−7.67	13.2	1.597	+0.41	−0.298	74
CN	0.66	−1.97	−8.20	−12.6	1.559	+0.45	−0.342	76
F	−0.07	−2.32	−9.65	1.1	1.594	+0.42	−0.321	73
Cl	0.11	−1.24	−8.50	−0.8	1.586	+0.42	−0.321	74
BCl$_2$	0.86	−1.33	−6.68	−8.8	1.568	+0.45	−0.329	76
SiCl$_3$	0.57	−1.62	−7.74	−9.7	1.568	+0.45	−0.329	76
PCl$_2$	0.62	−1.69	−7.71	−6.6	1.571	+0.43	−0.324	75

[a] Retrieved from Ref. 1.
[b] GIAO-B3LYP/6-311+G*//B3LYP/6-31G*.
[c] NICS values for aryl compounds (see Ref. 9).
[d] Calculated at B3LYP/6-31G*.
[e] According to Eq. (1) (see Ref. 9).
[f] Bird aromaticity index.

Inspection of the values in the Table 2 reveals good qualitative correlation ($r = 0.91$–0.99) between the aromaticity reflected in the NICS values (the more negative this value, the greater the aromaticity) the charge on the exocyclic carbon, exocyclic bond order, LUMO energy, resonance stabilization energy and the Bird aromaticity index (I_6). The aromaticity also follows the σ_p^+ value of the substituent with electron-withdrawing groups (σ_p^+ positive) leading to increased aromaticity compared to the unsubstituted cation. Most importantly we found a good linear correlation between our calculated magnetic and geometric aromaticity criteria (NICS and I_6 values) and the Hammett constants (σ_p^+)

allowing σ_p^+ values to be directly obtained from these theoretical calculations. Up to now it has proven difficult to make direct theoretical predictions of the Hammett constants.

Acknowledgements

Table 2. Correlation coefficients of regressions between Hammett constants $\sigma_p(+)$, NICSs, RSEs, NBO bond orders and charges, LUMO energies and I_6 for the considered aryl cations

Parameter	$\sigma_p(+)$	NICS	ΔE_{stb}	BO_{exo}	$q(C_{exo})$	E_{LUMO}	I_6
$\sigma_p(+)$	1.00						
NICS	0.92	1.00					
ΔE_{stb}	0.91	0.97	1.00				
BO_{exo}	0.89	0.91	0.93	1.00			
$q(C_{exo})$	0.91	0.97	0.97	0.96	1.00		
E_{LUMO}	0.91	0.96	0.99	0.95	0.98	1.00	
I_6	0.94	0.94	0.95	0.98	0.95	0.95	1.00

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$$PhCH_2^+ + Ar\text{-}CH_3 \rightarrow ArCH_2^+ + PhCH_3 \qquad (1)$$

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