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Note

Are the molecular non-covalent interactions of alkali cation-benzene (M^+-XC_6H_5) complexes confined to a specific carbon atom or propagated through space effects of the substituents? An intense reinvestigation using LFER

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The importance of potential use of Linear Free Energy Relationships (LFER, both Hammett and Taft equations) is explored by applying to the binding/interaction energies of the cation-benzene molecular complexes. An intense study of the application of both Hammett and Taft correlations in their various forms in the present study reveals that the substituent effect is not confined to a particular carbon atom of the π-system of benzene but propagated through the entire moiety of the π-system. Possible explanations are provided based on the magnitude of several Hammett and Taft reaction constants (ρ and ρ^*).

Keywords: Hammett equation, Taft equation, Binding energies, Interaction energies

Strong non-covalent molecular interactions or binding studies of alkali cations-benzene complexes are well investigated in detail owing to their importance in biology and chemistry[1-8]. Different lines of arguments were put forward for their formation and stability in terms of effect of substituents, electrostatic potentials of substituted benzenes, through-space effects of the substituents, aromatic polarization, and binding enthalpies. In one of the studies by Dougherty *et al.*[4], mentioned that the effect of substituents is due primarily to the inductive effects but not by any resonance contribution. In another instance by Wheeler *et al.*[5] is that the effect of substituents is space effects offered by substituents. In the present study we went a step ahead to apply LFER in their different forms not studied earlier. We have observed satisfactory correlations using different Hammett substituent parameters. In some cases, Taft correlations are also satisfactory. At the end it was shown that there exists also a good correlation between binding enthalpies of M^+-benzene (M = Li, Na, K, Rb and Cs) complexes and the ionization potentials and electron affinities of alkali metals using Feller's data[7].

Methods

All correlations were done using KaleidaGraph software, Reading, PA, USA. All the chemical structures were drawn using ChemDraw. All Hammett σ and Taft σ* values are from Refs. 9, 10 and 11.

Results and Discussion

As shown in Fig. 1, benzene is a good model of a π system. Due to its molecular symmetry and having weak polar carbon–hydrogen bonds it has no net permanent dipole moment. Yet, the face of the electron-rich π system above and below the benzene ring shows a partial negative charge. The positive charge associated with the plane of the benzene atoms is counterbalanced by the partial negative charge. This results in an electric quadrupole with a pair of dipoles, aligned like a parallelogram. Therefore, there is no net molecular dipole moment. The negatively charged region of the quadrupole above and below the plane of the molecule can effectively interact with cations like alkali metals with high charge density associated with them. This is the best example of a noncovalent molecular bonding between a monopole (cation) and a quadrupole (π system). Fig. 2 is the benzene ring with a substituent.

If X is electron donating, *meta* position is electron deficient, *ortho* and *para* positions are electron rich as shown in Scheme 1.

Therefore M^+ will be attracted by *ortho* and *para* carbons as shown in Fig. 3.

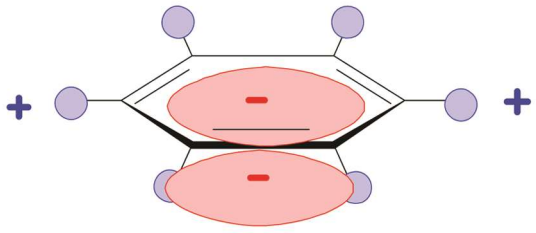
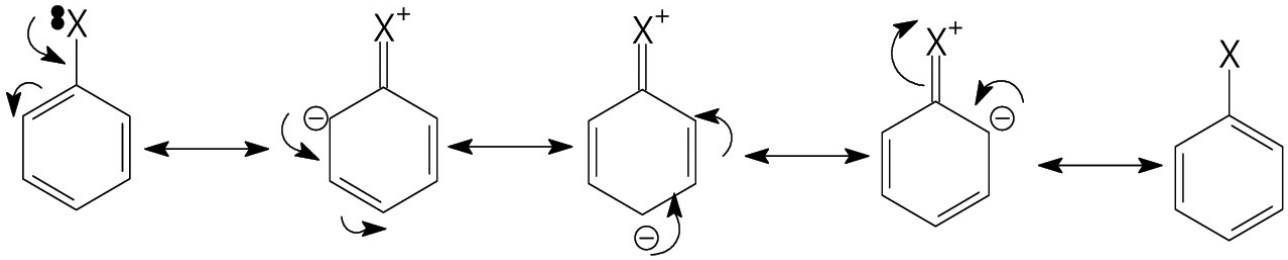
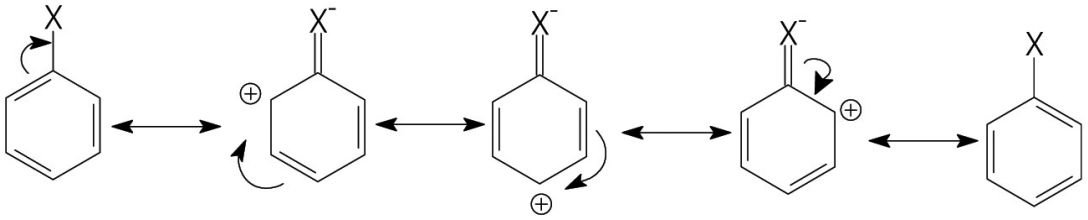


Fig. 1



Scheme 1



Scheme 2

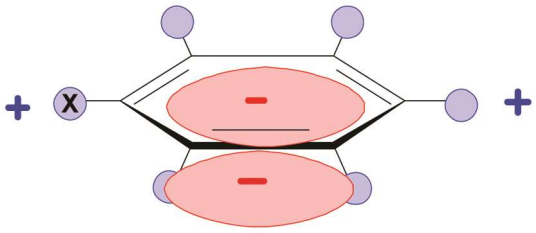


Fig. 2

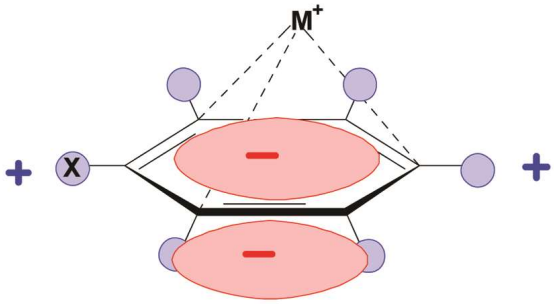


Fig. 3

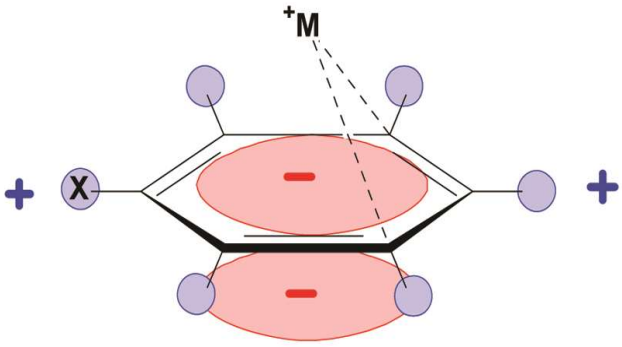


Fig. 4

If X is electron withdrawing, *meta* position is electron rich, *ortho* and *para* positions are electron deficient as shown in Scheme 2.

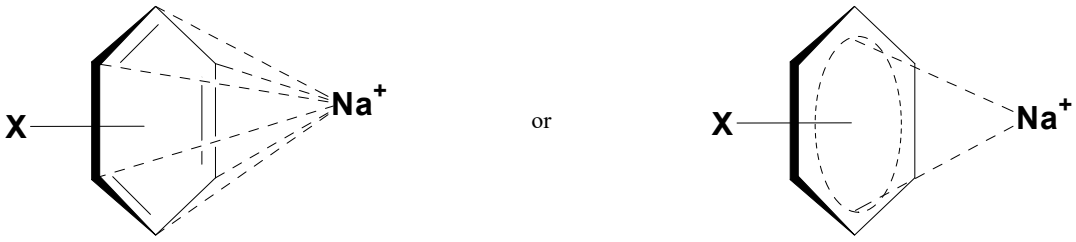
Therefore M^+ will be attracted by *meta* carbons as shown in Fig. 4.

In order to explore the effect of substituent X on the non-covalent interaction of M^+ - π-system as shown in Fig. 3 and Fig. 4, Hammett equation in its various forms and Taft equation are applied on the binding energy data and interaction energy data. Table 1 shows the binding energy data of Na^+ - benzene COMPLEX.

In the studies by Dougherty *et al.*[4], mentioned that the effect of substituents is due primarily to the inductive effects by the substituents based on the σ_m, and σ_m^+ but not by any resonance contribution. In fact, we have reaffirmed the same in this study using σ_m^- also, where the Hammett correlations are good with σ_m, σ_m^+ and σ_m^- with $R > 0.96$ (Table 2).

But at the same time, one cannot completely rule out the systematic resonance contribution of the substituents from *ortho* and *para* positions as pointed out by Dougherty *et al.*[4]. In fact, the Hammett (Table 2) and Taft (Table 2) correlations with *para* and *ortho* substituent constants though not satisfactory ($R > 0.82$ except correlation with σ_p^-) but the trends are not misleading. Therefore, one can conclude that the effect of substituents on binding energies of Na^+-benzene complexes is not confined to a particular carbon, but it is an overall collective contribution from all the carbons with a minor

Table 1 — Binding energy (BE) values of Na^+ - Benzene complex (*J Am Chem Soc*, 118 (1996) 2307-2308 (https://doi.org/10.1021/ja9539608)



Sl. No.	X	Hammett σ/Taft σ^*_{ortho}							BE (Na^+ - Benzene) kcals/mol
		σ_{para}	σ_{meta}	σ^*_{ortho}	σ^+_{para}	σ^+_{meta}	σ^-_{para}	σ^-_{meta}	
1	H	0.00	0.00	0.49	0.00	0.00	0.00	0.00	–27.1
2	F	0.06	0.34	3.21	–0.07	0.35	0.06	0.41	–22.0
3	OH	–0.37	0.12	1.34	–0.92	0.04	–0.11	0.17	–26.9
4	NH_2	–0.66	–0.16	0.62	–1.30	–0.16	–0.30	–0.04	–31.8
5	Cl	0.23	0.37	2.96	0.11	0.40	0.27	0.45	–21.5
6	CN	0.66	0.56	3.30	0.66	0.56	0.91	0.68	–15.7
7	BH_2	0.43	0.30	1.87	0.43	0.15	1.02	0.26	–24.4

Table 2 — Summary of Hammett/Taft reactions constants Na^+ - Benzene complex

Sl. No.	Correlation	Hammett/Taft Reaction constants ρ or ρ^*	Correlation coefficient (R)
1	BE vs Hammett σ_p	$\rho_p = 9.98$	0.8814
2	BE vs Hammett σ_m	$\rho_m = 20.3$	0.9712
3	BE vs Taft σ^*_{ortho}	$\rho^*_{ortho} = 3.80$	0.8895
4	BE vs Hammett σ^+_p	ρ^+_p =6.00	0.8297
5	BE vs Hammett σ^+_m	$\rho^+_m = 19.8$	0.9807
6	BE vs Hammett σ^-_p	$\rho^-_p = 7.04$	06994
7	BE vs Hammett σ^-_m	$\rho^-_m = 19.3$	0.9689

Table 3 — Interaction energy values (E_{int}) of Na^+ - Benzene (XC_6H_5) complex

Steven E. Wheeler and K. N. Houk, *J Am Chem Soc*, 131 (2009) 3126–3127

Sl. No.	X	Hammett σ/Taft σ^*_{ortho}							E_{int}/kcals
		σ_{para}	σ_{meta}	σ^*_{ortho}	σ^+_{para}	σ^+_{meta}	σ^-_{para}	σ^-_{meta}	
1	$N(CH_3)_2$	–0.83	–0.20	0.32	–1.70	–	–0.18	–0.17	33.9
2	$NH(CH_3)$	–0.84	–0.30	–0.89	–	–	–	–	33.1
3	NH_2	–0.66	–0.16	0.62	–1.30	–0.16	–0.30	–0.04	31.8
4	CH_2OH	0.08	0.08	0.31	–	–	–	–	29.5
5	NHOH	–0.34	–0.04	0.30	–	–	–	–	29.1
6	SCH_3	0.00	0.15	1.56	–	–	–	–	28.6
7	OCH_3	–0.27	0.12	1.81	–0.78	0.05	–0.19	0.11	28.5
8	CH_3	–0.17	–0.07	0.00	–0.31	–0.10	–0.14	0.02	28.3
9	H	0.00	0.00	049	0.00	0.00	0.00	0.00	26.9
10	OH	–0.37	0.12	1.34	–0.92	0.04	–0.11	0.17	26.6
11	SH	0.15	0.25	1.68	–	–	–	–	26.3
12	SiH_3	0.10	0.05	0.72	0.06	0.11	0.26	0.10	26.0
13	C≡CH	0.23	0.21	2.18	0.15	0.29	0.47	0.35	25.4
14	CO_2CH_3	0.39	0.32	2.00	0.48	0.37	0.76	0.33	23.6
15	$COCH_3$	0.50	0.38	1.65	0.30	0.27	0.80	0.32	22.2
16	F	0.06	0.34	3.21	–0.07	0.35	0.06	0.41	21.8
17	COOH	0.43	0.36	2.08	0.42	0.32	0.84	0.42	21.5

(*contd.*)

Table 3 — Interaction energy values (E_{int}) of Na^+ - Benzene (XC_6H_5) complex (*contd.*)

Steven E. Wheeler and K. N. Houk, *J Am Chem Soc*, 131 (2009) 3126–3127

Sl. No.	X	Hammett σ/Taft σ^*_{ortho}							
		σ_{para}	σ_{meta}	σ^*_{ortho}	σ^+_{para}	σ^+_{meta}	σ^-_{para}	σ^-_{meta}	
18	OCF_3	0.35	0.40	2.33	–	–	–	–	20.7
19	BF_2	0.48	0.32	1.96	0.49	0.25	0.76	0.33	20.2
20	CHO	0.22	0.36	2.15	0.47	0.39	1.00	0.45	19.7
21	CF_3	0.54	0.43	2.61	0.53	0.44	0.66	0.50	19.4
22	SiF_3	0.69	0.54	2.98	–	–	–	–	18.5
23	NO	0.91	0.62	3.35	0.61	0.53	1.70	0.63	17.4
24	CN	0.66	0.56	3.30	0.66	0.56	0.91	0.68	16.0
25	NO_2	0.78	0.71	4.00	0.79	0.73	1.30	0.78	14.0

Table 4 — Summary of Hammett/Taft reactions constants

		Na^+ - Benzene complex	
Sl. No.	Correlation	Hammett/Taft Reaction constants ρ or ρ^*	Correlation coefficient (R)
1	E_{int} vs Hammett σ_p	$\rho_p = -10.3$	0.9178
2	E_{int} vs Hammett σ_m	$\rho_m = -19.7$	0.9599
3	E_{int} vs Taft σ^*_{ortho}	$\rho^*_{ortho} = -3.95$	0.8927
4	E_{int} vs Hammett σ^+_p	$\rho^+_p = -6.67$	0.9068
5	E_{int} vs Hammett σ^+_m	$\rho^+_m = -19.0$	0.9523
6	E_{int} vs Hammett σ^-_p	$\rho^-_p = -8.08$	0.8720
7	E_{int} vs Hammett σ^-_m	$\rho^-_m = -19.7$	0.9660

Table 5 — Interaction energy values (E_{int}) of Li^+/Na^+ - Alkylbenzene (RC_6H_5) complex

Sl. No.	R	Hammett σ/Taft σ^*_{ortho}							E_{int}/kcals
		σ_{para}	σ_{meta}	σ^*_{ortho}	σ^+_{para}	σ^+_{meta}	σ^-_{para}	σ^-_{meta}	
					Li^+ - RC_6H_5 complex				
1	H	0.00	0.00	0.49	0.00	0.00	0.00	0.00	–35.6
2	CH_3	–0.17	–0.07	0.00	–0.31	–0.10	–0.14	0.02	–38.3
3	C_2H_5	–0.15	–0.07	–0.10	–	–	–	–	–38.7
4	t-Bu	–0.20	–0.10	–0.30	–0.34	–0.14	–0.12	–0.06	–40.2
					Na^+ - RC_6H_5 complex				
1	H	0.00	0.00	0.49	0.00	0.00	0.00	0.00	–21.6
2	CH_3	–0.17	–0.07	0.00	–0.31	–0.10	–0.14	0.02	–23.4
3	C_2H_5	–0.15	–0.07	–0.10	–	–	–	–	–23.8
4	t-Bu	–0.20	–0.10	–0.30	–0.34	–0.14	–0.12	–0.06	–24.8

degree of differences. No doubt the correlation with *meta* substituents constants is good[4].

However, not to ignore, in another instance by Wheeler *et al*.[5] is that the effect of substituents is space effects offered by substituents. This may be the reason that the interaction energies of Na^+ - benzene (XC_6H_5) complexes follow the correlations with all Hammett and Taft substituent constants (Table 3 and Table 4). All the correlation coefficients are > or ≈ 0.89 Table 4).

Similarly same trends are observed for the Li^+/Na^+ - Alkylbenzene (RC_6H_5) complexes (Table 5 and Table 6) except the correlation with σ^-_m.

Therefore, the interaction can be as shown in Scheme 3.

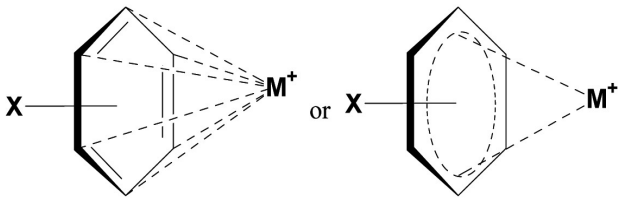
Also, there is a good correlation between the binding energy (BE) of alkali metal cation-benzene complexes and ionization energy and electron affinities of the cations (Table 7). Therefore, we conclude that the polarization of the

Table 6 — Summary of Hammett/Taft reactions constants Li^+/Na^+ - Alkylbenzene (RC_6H_5) complexes

Sl. No.	Correlation	Hammett/Taft Reaction constants ρ or ρ^*	Correlation coefficient (R)
		Li^+ - Alkylbenzene (RC_6H_5) complex	
1	E_{int} vs Hammett σ_p	ρ_p = 20.7	0.9607
2	E_{int} vs Hammett σ_m	ρ_m = 44.8	0.9920
3	E_{int} vs Taft σ^*_{ortho}	ρ^*_{ortho} = 5.69	0.9968
4	E_{int} vs Hammett σ_p^+	ρ_p^+ = 11.6	0.9415
5	E_{int} vs Hammett σ_m^+	ρ_m^+ = 31.7	0.9899
6	E_{int} vs Hammett σ_p^-	ρ_p^- = 25.9	0.8494
7	E_{int} vs Hammett σ_m^-	ρ_m^- = 36.0	0.6477
		Na^+ - Alkylbenzene (RC_6H_5) complex	
1	E_{int} vs Hammett σ_p	ρ_p = 14.3	0.9519
2	E_{int} vs Hammett σ_p	ρ_m = 31.1	0.9875
3	E_{int} vs Taft σ^*_{ortho}	ρ^*_{ortho} = 3.97	0.9969
4	E_{int} vs Hammett σ_p^+	ρ_p^+ = 7.94	0.9317
5	E_{int} vs Hammett σ_m^+	ρ_m^+ = 21.9	0.9855
6	E_{int} vs Hammett σ_p^-	ρ_p^- = 17.7	0.8343
7	E_{int} vs Hammett σ_m^-	ρ_m^- = 25.8	0.6688

Table 7 — Binding energy (BE) of alkali metal cation-benzene complexes MP2 (6-311+G*)

Sl. No.	Metal ion	Ionization energy $kjmol^{-1}$	Electron affinity $kjmol^{-1}$	BE kcals
1	Li^+	520.2	59.62	–36.0
2	Na^+	495.8	52.87	–21.9
3	K^+	418.8	48.38	–16.7
4	Rb^+	403.0	46.89	–13.9
5	Cs^+	375.7	45.51	–12.1



Scheme 3

π-system is systematically affected by the electron affinities and ionization energies of the cations.

Conclusions

A detailed reinvestigation is carried out using LFER on the molecular non-covalent interactions of alkali cation-benzene (M^+-XC_6H_5) complexes. We have shown that the effect of substituents is not confined to a specific carbon atom of π-framework of the benzene ring, but it is propagated through space effects of the substituents.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

Conflict of interest statement

The authors do not have any conflict of interest.

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