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Supplementary Material

Experimental and Quantum Mechanical Study of Nucleophilic Substitution Reactions of *meta* and *para*-Substituted Benzyl Bromides with Benzylamine in Methanol Medium: Synergy Between Experiment and Theory

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Supplementary Material - Part 1

Results for Gas-Phase

Table 1: Bond lengths (in Angstroms) of Benzyl amine (BA) – Benzyl bromide (BB) transition state in gas phase

Substi-tuent (X) in BB	Hammett's σ	C-Br of TS (bond breaking) Fig. 1	N-C of TS (bond forming) Fig. 2	Avg. Bond lengths of aromatic ring (BB) Fig. 3	Charge on N Fig. 4	Charge on Br Fig. 5
4-CH_3	-0.17	2.66133	1.96097	1.392125	- 0.686	-0.685
3-CH_3	-0.07	2.6544	1.9531	1.392002	-0.683	-0.679
H	0	2.64882	1.95448	1.391335	-0.684	-0.675
4-Cl	0.23	2.64538	1.94865	1.389895	-0.682	-0.67
4-NO_2	0.78	2.62021	1.93128	1.389197	-0.676	-0.636

With regard to the absolute value of Hammett's reaction constant rho, it is larger for the C-Br bond breaking step (Fig. 1) than for N-C (Fig. 2) bond formation step. Hence the C-Br bond breaking step is more sensitive to the substituent affect than the N-C bond formation is. Again the rho value for charge development on N (Fig. 4) is more than charge development on Br (Fig 5); hence the charge formation on N is more sensitive to the substituent affect than the charge formation on the Br is. . The foregoing two trends are unlike the trends in methanol medium where the rho value is larger for N-C bond formation step, and for charge development on Br.

Figure 1: C-Br bond length vs Hammett σ in gas-phase

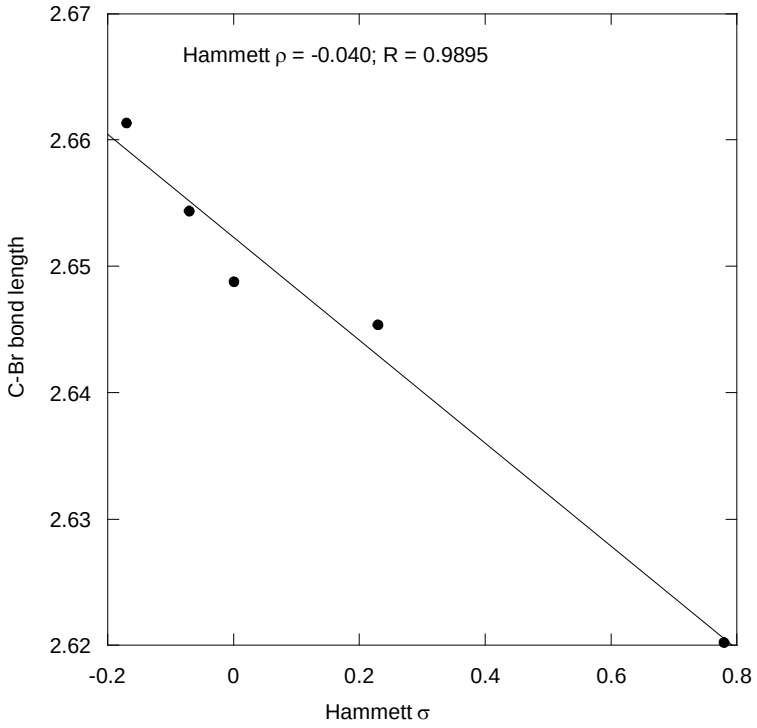


Figure 2: N-C bond lenth vs Hammett σ in gas-phase

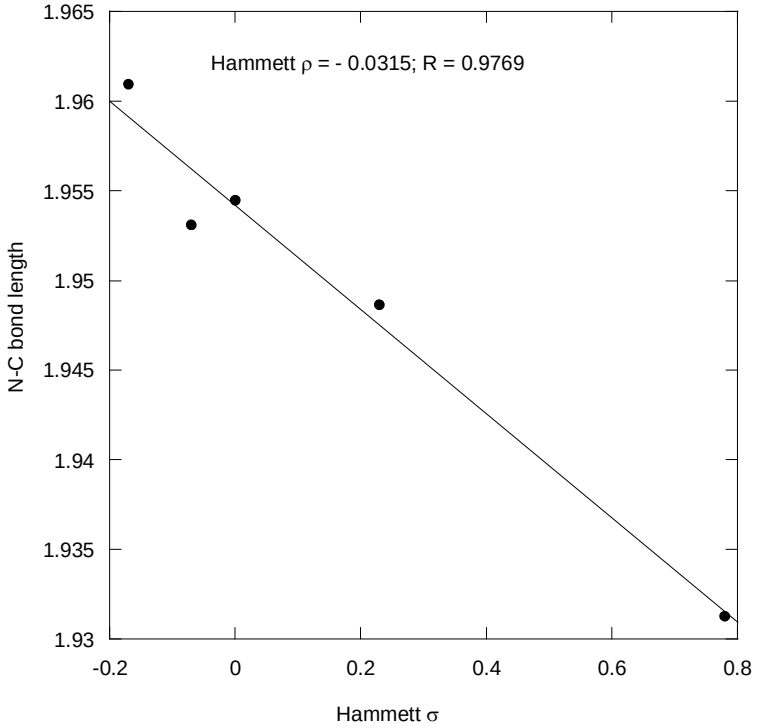


Figure 3: Average aromatic bond length vs Hammettσ in gas-phase

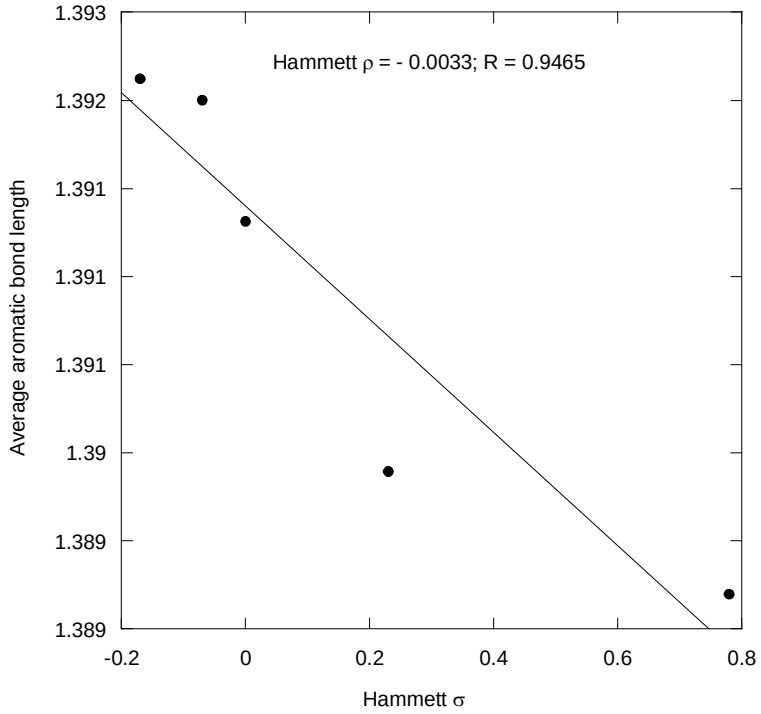


Figure 4: Charge on Nitrogen vs Hammettσ in gas-phase

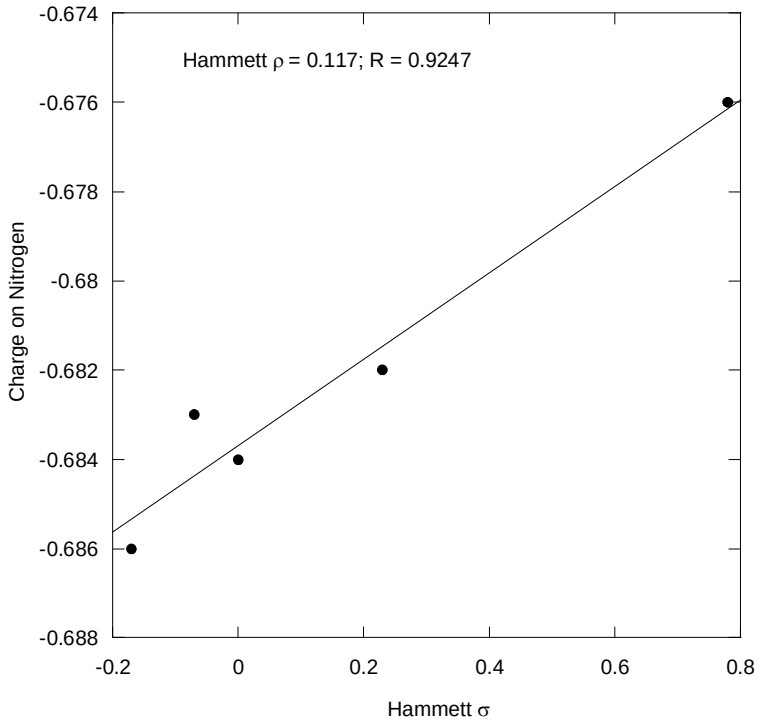
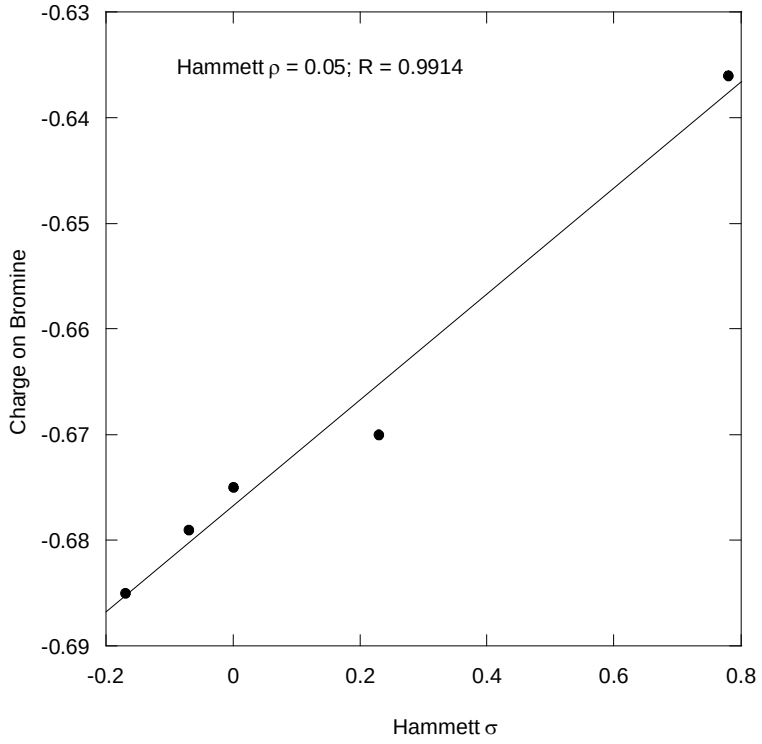


Figure 5: Charge on bromine vs Hammett σ in gas-phase



Supplementary Material – Part 2

Table 2: Stabilization energy associated with donor-acceptor (bond-antibond) interactions in the NBO basis in kcal/mol (gas phase)

Substituent (Y)	Hammett's (σ)	Donor NBO(LP) = N Acceptor NBO(LP*) = C i.e. Benzyllic carbon of BB in kcal/mol Fig. 6	Donor NBO(LP) = Br Acceptor NBO(LP*) = C i.e. Benzyllic carbon of BB in kcal/mol Fig. 7
4-MeO	-0.27	185.91	108.25
3-Me	-0.17	186.42	109.48
H	0.00	186.72	110.22
4-Cl	0.23	187.62	112.5
4-CF_3	0.54	190.04	118.18

Figure 6: Plot of Donor NBO(LP) = N to Acceptor NBO(LP*) = C versus Hammett σ

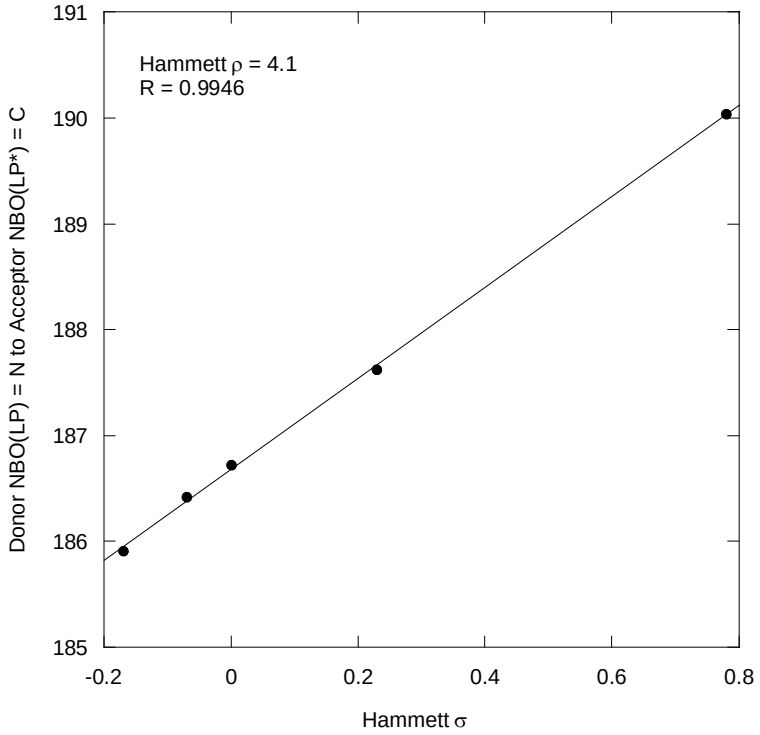
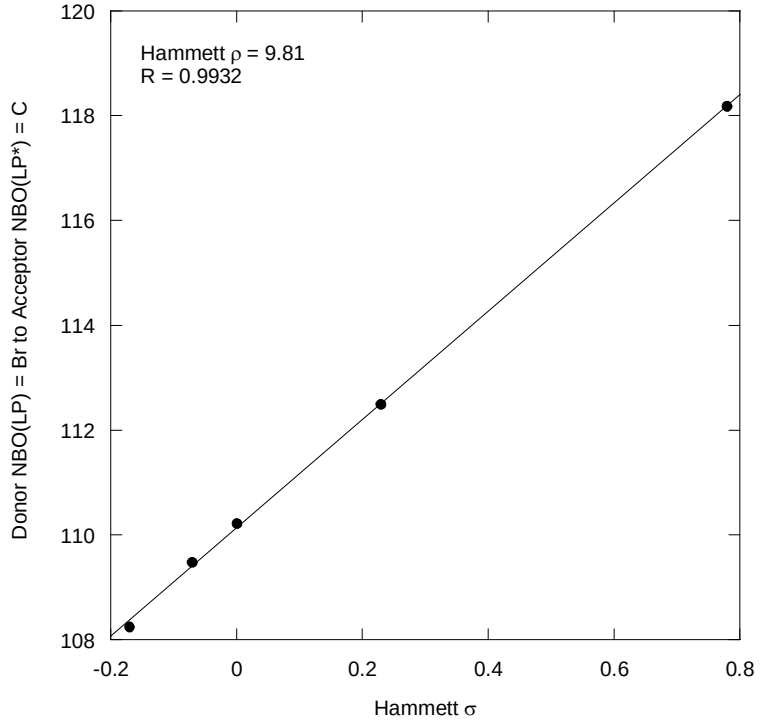


Figure 7: Plot of Donor NBO(LP) = Br to Acceptor NBO(LP*) = C versus Hammett σ



Supplementary Material – Part 3

HOMO-LUMO TRANSITION STATE (GAS PHASE)

Similar to the methanol phase energy levels of HOMO and the LUMO (Table3) of the Transition state conform to Hammett's relation. The absolute reaction constant or the rho value for LUMO (Figure9) is larger than for HOMO (Figure 8). This again does reflect that the substituent effect is more sensitive to LUMO energy levels than HOMO energy levels.

Table 3 (Gas Phase)

Substituent at BB of the Transition State	Hammett's s	HOMO of the Transition State kcal/mol Fig 8	LUMO of the Transition State kcal/mol Fig 9
p-methyl	-0.17	-164.457718	3.2818753
m-methyl	-0.07	-165.355057	2.9241948
H	0	-166.371622	2.2715848
p-chloro	0.23	-169.12639	-1.68172575
p-nitro	0.78	-176.411776	-25.6337675

Figure 8: Hammett's s vs HOMO of the TS (Gas Phase)

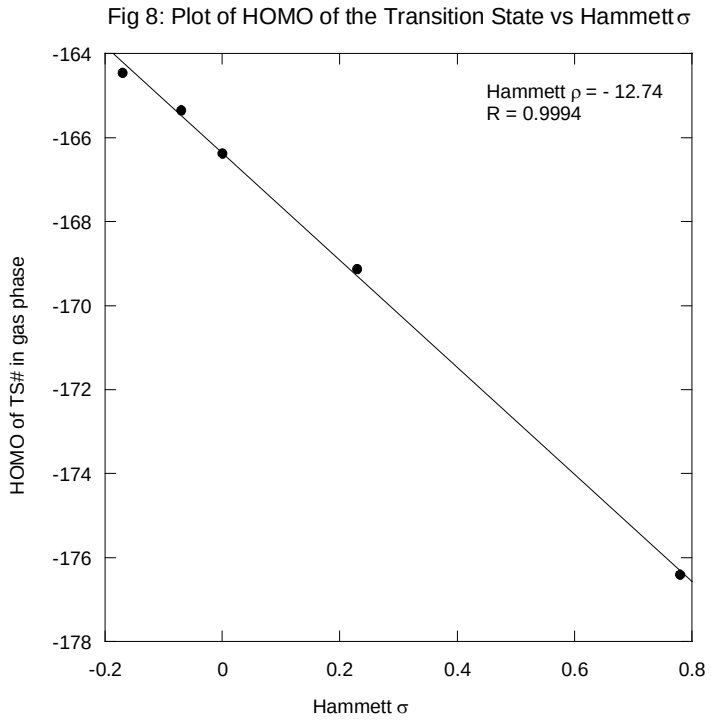


Figure 9: Hammett's s vs LUMO of the TS (Gas Phase)