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Steric effects of nucleophile-radical coupling reaction. Determination of rate constants for the reaction of aryl radicals with 2-naphthoxide anion

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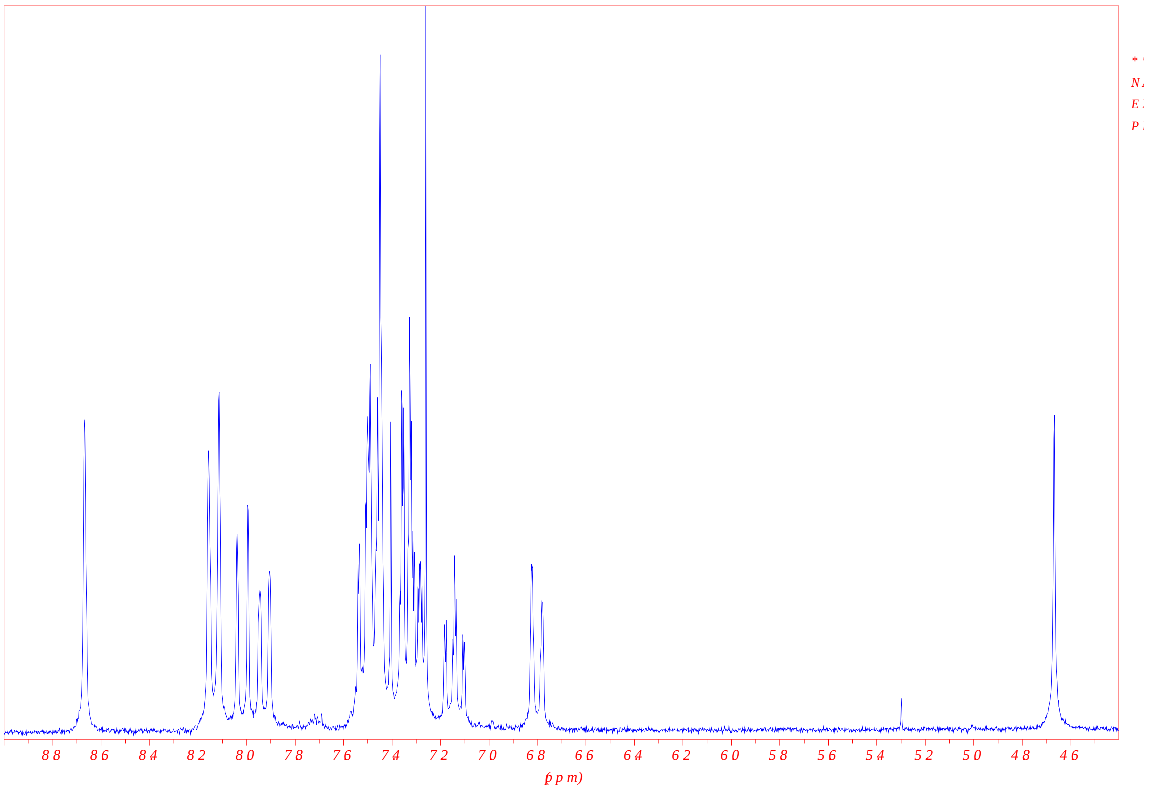
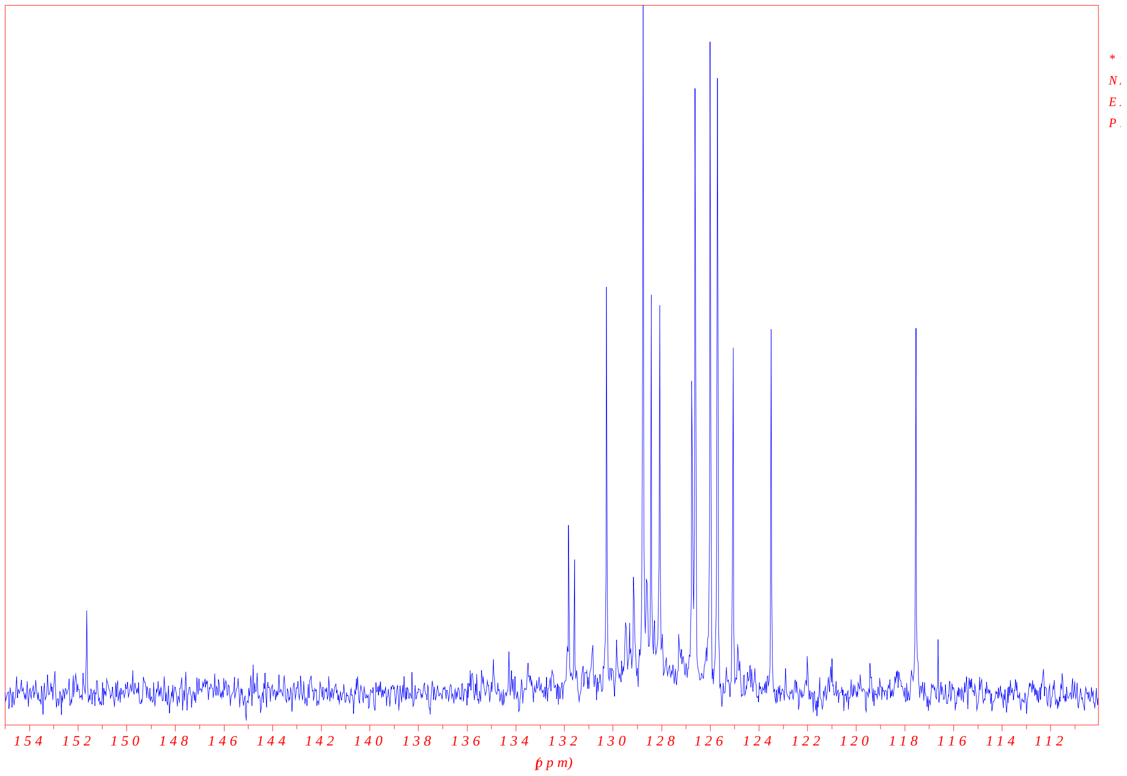
Electronic Supplementary Information (ESI)

^{1}H NMR and ^{13}C NMR spectra of compounds ***3e****.*

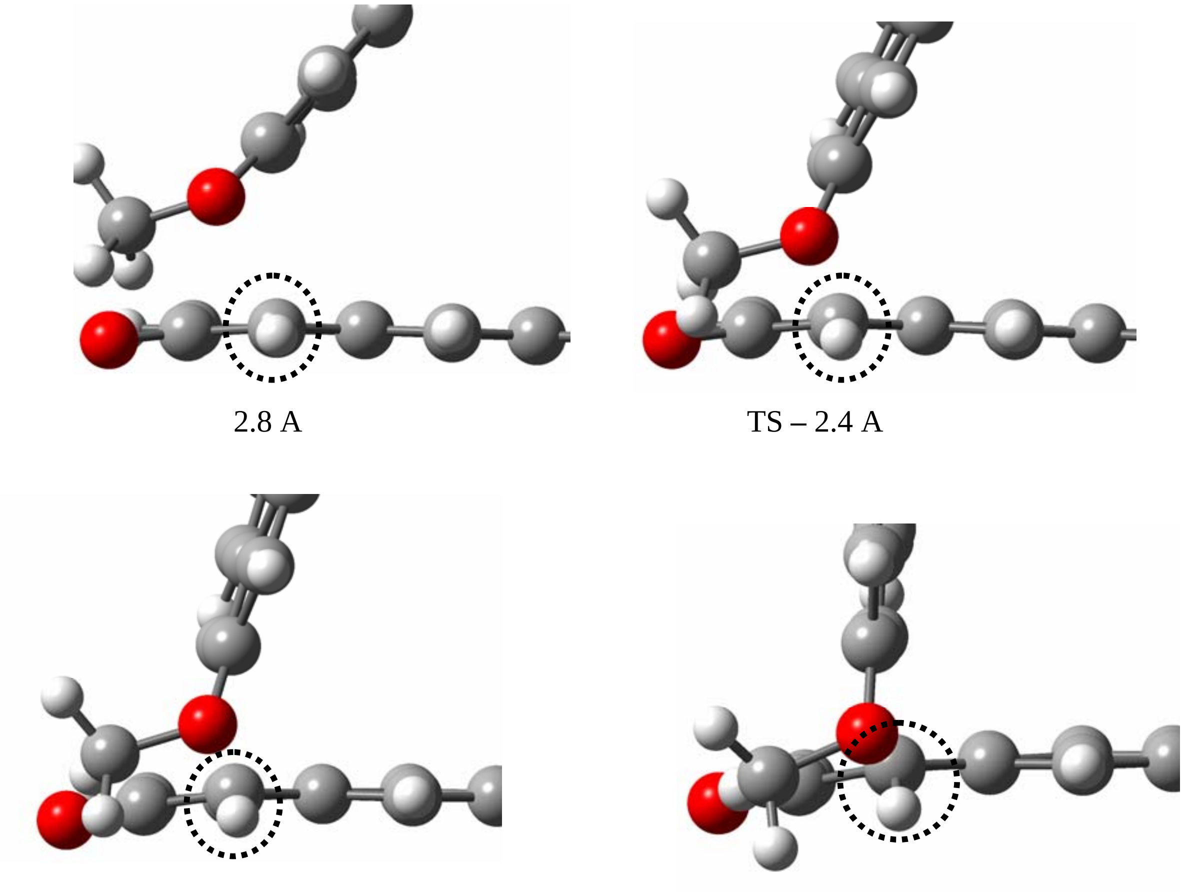




Computational procedure

All calculations were carried out with the semiempirical AM1 and B3LYP methods as implemented in Gaussian 03 within the UHF(opened shell systems) or RHF(closed shell systems) formalisms in order to properly account for the electronic nature of the species under study. First, the most stable conformers of the radical anions $RNu^{-\cdot}$ were evaluated through an AM1 conformational search by scanning the two or three main torsion angles. The conformers thus obtained were then refined with complete geometry optimization. The geometries thus found were used as starting points to study the PEs corresponding to the C-C bond breaking/formation. The equilibrium geometries were obtained with complete geometry optimization. The intermediates and transition states were first located through the reaction coordinate method and then refined with the appropriate procedure. The stationary points were located by Hessian matrix calculations: all positive eigenvalues for a minimum energy species and one imaginary frequency for transition states. PEs explorations within the B3LYP DFT functional and the 6-31G* basis set were carried out by the same procedure. The solvent effect was modeled with a continuum model as implemented in the G03 program. The solvent stabilization was evaluated from single point calculations on the gas-phase optimized geometries at the B3LYP/6-31G* theory level; eletrostatic and non-electrostatic contributions being considered.

Figure ESI 1: The hybridization change (sp^2 to sp^3) in reaction path, for the coupling of 2-naphthoxide anion and 2-methoxy-1-naphthyl radical.



2.8 A

TS – 2.4 A

2.3 A

2.0 A

Table ESI 1. The energy of PES relevant points of the reaction of the anion of ***1*** *with different aryl radicals.*

Anion of 2-naphthol + 4-anisyl radical (**2a**)

		Distance C1-radical centre	Energy (Hartree)	Solvatation Energy (kcal/mol)	ΔE^a (kcal/mol)	ΔETS-IT (kcal/mol)
Product	Gas phase	1.53856	-806,6865077		-36,5555032	
	solution		-806,7684817	-51,4394638	-33,0338571	
TS	Gas phase	3.00375	-806,6354174		-4,49585456	1,6018868
	solution		-806,7178855	-51,7495162	-1,28426094	0,46931436
IT	Gas phase	5.34683	-806,6380193		-6,09774136	
	solution		-806,7186334	-50,6169438	-1,7535753	
Reactives (15 A)	Gas phase		-806,6282528			
	solution		-806,7158389	-54,9611098		

$^a\Delta E$ = energy difference between transition states and reactants (anion of **1** + radical, distance = 15 Å).

Anion of 2-naphthol + 2-anisyl radical (**2b**)

		Distance C1-radical centre	Energy (Hartree)	Solvatation Energy (kcal/mol)	ΔE^a (kcal/mol)	ΔE_{TS-IT} (kcal/mol)
Product	Gas phase	1.53108	-806,6877749		-32,9834681	
	solution		-806,7658848	-49,0147043	-30,5499235	
TS	Gas phase	2.46068	-806,6382664		-1,91641401	0,12838844
	solution		-806,7147711	-48,007426	1,52440883	1,99623322
IT	Gas phase	5.68453	-806,638471		-2,04480246	
	solution		-806,7179523	-49,8752708	-0,47182439	
Reactives (15 A)	Gas phase		-806,6352124			
	solution		-806,7172004	-51,4482489		

$^a\Delta E$ = energy difference between transition states and reactants (anion of **1** + radical, distance = 15 Å).

Anion of 2-naphthol + 1-naphthyl radical (**2c**)

		Distance C1-radical centre	Energy (Hartree)	Solvatation Energy (kcal/mol)	ΔE[a] (kcal/mol)	ΔE_{TS-IT} (kcal/mol)
Product		1.53011	-845,8088519		-34,9701632	
	solution		-845,887836	-49,5632731	-30,5207443	
TS		2.50742	-845,7624239		-5,8361521	0,02453562
	solution		-845,8408655	-49,2228492	-1,04630934	0,35178183
IT		2.66203	-845,762463		-5,86068773	
	solution		-845,8414261	-49,5500954	-1,39809117	
Reactives (15 A)			-845,7531234			
	solution		-845,8391981	-54,01269196		

[a] ΔE = energy difference between transition states and reactants (anion of **1** + radical, distance = 15 Å).

Anion of 2-naphthol + 2-metoxy-1-naphthyl radical (**2d**)

		Distance C1-radical centre	Energy (Hartree)	Solvatation Energy (kcal/mol)	ΔE[a] (kcal/mol)	ΔE_{TS-IT} (kcal/mol)
Product		1.53231	-960,3288457		-29,8186239	
	solution		-960,4072327	-49,18858718	-28,0464116	
TS		2.4464	-960,2834098		-1,30716504	1,6778349
	solution		-960,3589759	-47,41844563	2,23518884	2,92174698
IT		3.8922	-960,2860836		-2,98499994	
	solution		-960,363632	-48,66235771	-0,68655814	
Reactives (15 A)			-960,2813267			
	solution		-960,3625379	-50,96079951		

[a] ΔE = energy difference between transition states and reactants (anion of **1** + radical, distance = 15 Å).

Table 2 ESI. Energy differences between PES relevant points of the reaction of the 2-naphthoxide anion with different aryl radicals calculated for different solvents.

Radical		Solvatation Energy (kcal/mol)			ΔE[a] (kcal/mol)	ΔE_{TS-IT} (kcal/mol)	Products %[b]	
		TS	IT	Reactives			ArH	ArNu
3a	Gas phase				-4,50	1,60		
	DMSO	-51,75	-50,62	-54,96	-1,28	0,47	7	54
	CH_3OH[c]	-51,59	-50,49	-54,77	-1,32	0,54	13	42
3b	Gas phase				-1,92	0,13		
	DMSO	-48,00	-49,87	-51,44	1,52	1,99	15	40
	CH_3OH[c]	-47,91	-49,56	-50,86	1,04	1,78	---	---
3c	Gas phase				-5,84	0,02		
	DMSO	-49,22	-49,55	-54,01	-1,04	0,35	10	65
	CH_3OH[c]	-48,91	-49,29	-53,38	-1,36	0,41	20	53
3d	Gas phase				-1,31	1,68		
	DMSO	-47,42	-48,66	-50,96	2,24	2,92	46	35
	CH_3OH[c]	-47,46	-48,49	-50,35	1,59	2,71	56	35

[a] ΔE = energy difference between transition states and reactants (anion of 1 + radical, distance = 15 Å.

[b] In DMSO, the relation [Nu$^-$]/[ArX] = 10. In NH_3 (Methanol calculations), the relation [Nu$^-$]/[ArX] = 2.

[c] Protic solvent with dielectric constant more similar to that liquid ammonia.