Asian Journal of Chemistry; Vol. 33, No. 2 (2021), 447-452

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23092

Can Aromaticity of Fused Aromatic Ring in 1,3-Pentadiene Modulate its Reactivity towards [1,5]-Halo Shift? - A DFT Study

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Received: 5 December 2020; *Accepted*: 26 December 2020; *Published online*: 15 January 2021; AJC-20233

In (*Z*)-1,3-pentadienes, [1,5]-H migration is suprafacially allowed while fluorine shift in this system takes place by a Contra Hoffmann antarafacial pathway for which aromaticity is the driving force. If aromaticity of the transition structure (TS) can drive a reaction towards a disallowed pathway as found in the case of fluorine, the role of aromatic ring annealed to (*Z*)-1,3-pentadienes in determining the reaction pathway and barrier is worth noting. Hence, the combined role of aromaticity of transition state and the loss in aromaticity of the annealed ring has been explored during the [1,5]-X (X = H, F, Cl, Br) shifts in aromatic (benzene/naphthalene) annealed 1,3-pentadiene system. Notable correlations between various aromaticity index NICS(0,1) with activation barriers show that aromaticity of transition structure in pericyclic reaction can drive the stereochemical course of a reaction. The distinct effect of fluorine to other halogens is the antara migration while the other halogens (Cl & Br) prefer supramode.

Keywords: Aromaticity, DFT study, Nucleus independent chemical shift, Supra/antarafacial mode, [1,5]-Halogen shift.

INTRODUCTION

The study of concerted processes in organic chemistry has been continually explored since the development of the general theory of orbital symmetry by Woodward & Hoffmann [1-10]. It is generally accepted that [1,5]-shift usually proceeds by a suprafacial concerted pathway involving an aromatic transition state [11-27] as rationalized by Woodward and Hoffmann [W-H] rule [28-31]. Further, the [1,5]-shifts in cyclic alkenes like cyclo-pentadiene, cyclopropene and cycloheptatriene have also been experimentally and theoretically explored [32,33]. Although generally carbon and hydrogen shifts are well known, migration of halogens have also been documented [10,13,30,34-36].

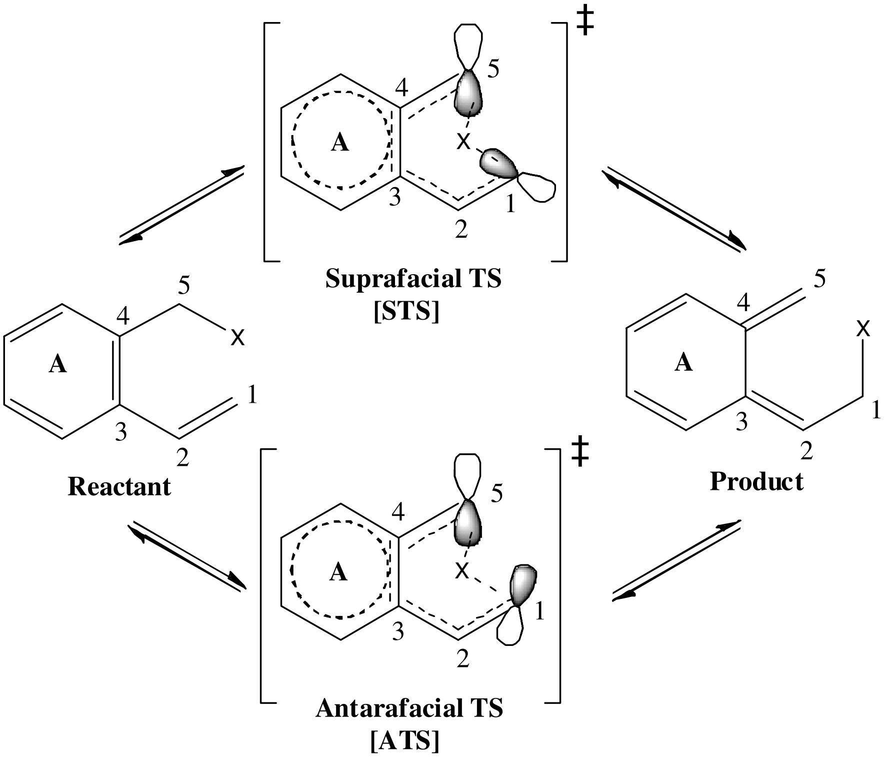
The aromaticity is a dynamic phenomenon which would facilitate the pericyclic reaction by its enhancement in the transition state [27]. Recently, during [1,5]-halo shift in 1,3-pentadiene [37], a contra Woodward Hoffmann allowed antarafacial pathway was noticed for [1,5]-F shift and amply supported on the basis of aromaticity. The present paper tries to further elaborate the role of aromaticity in this [1,5]-halo shifts in 1,3-pentadienes systems with aromatic benzene and naphthalene ring fused at 3,4-positions (benza and naphtha fused systems). The present study would evaluate the subtle competition in aromaticity of the ring and the transition state in deciding the reaction pathway and barrier to [1,5] shifts of X in the system under study.

COMPUTATIONAL METHODS

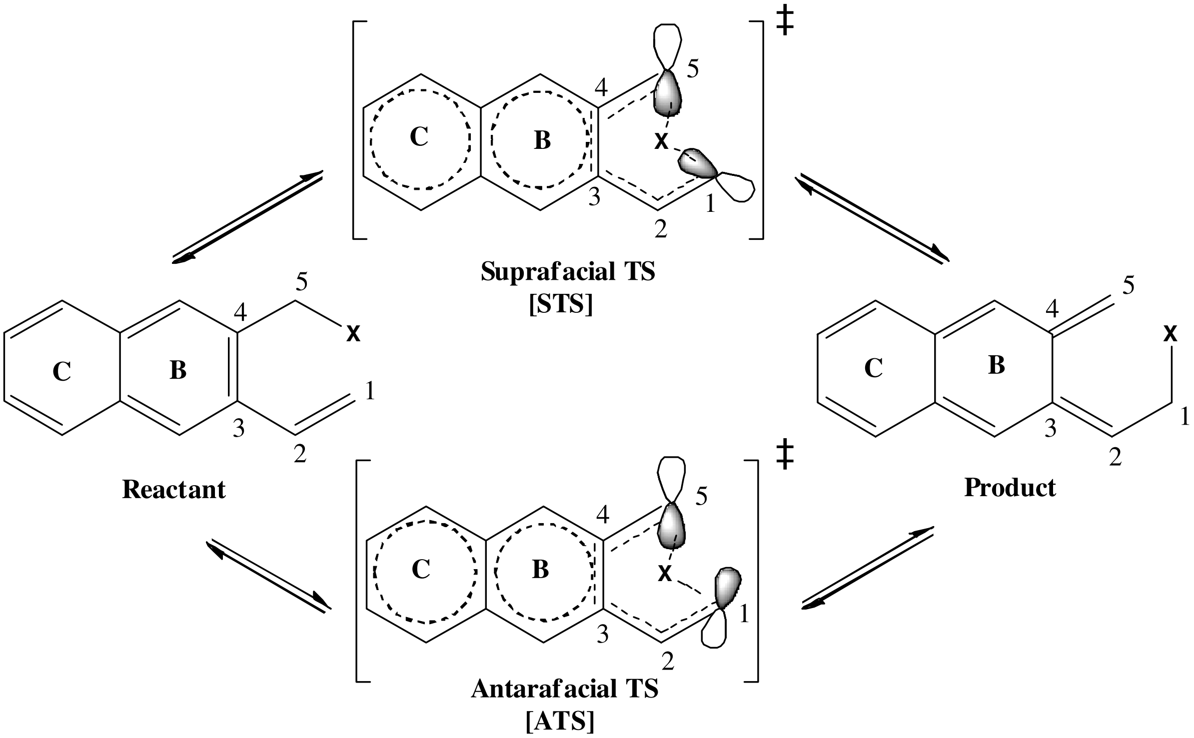
In this study, all the geometries were modelled and optimized at B3LYP [38-40]/6-31G(d,p) [38-40] level using Gaussian 98 software [41]. The optimized geometries of the reactants (R) and products (P) were characterized by real frequencies and transition states (TS) have one imaginary frequency corresponding to [1,5]-X migration. The intrinsic reaction coordinate (IRC) paths have also been calculated, which connected the TS with reactant and product. Thermo-chemical activation parameters like $\Delta E^{\ddagger}$, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated. Aromaticity index *viz.*, nucleus independent chemical shift (NICS) [42] values at the centre of the cyclic transition states & aromatic rings and 1 Å above and below the rings (NICS(0) and NICS(1), respectively) were computed using the gauge invariant atomic orbital (GIAO) [43,44] method at B3LYP/6-311G+(d,p) level.

RESULTS AND DISCUSSION

[1,5]-Shift of benz and naphtha fused pentadiene systems (BP(X) & NP(X) X = H/F/Cl/Br) (**I-VIII**) are modelled and transition states corresponding to two stereochemical pathways such as suprafacial [S] and antarafacial [A] modes are located (**Schemes I** and **II**). But for BP(H) & NP(H) only supramode TS is presented as the other antara mode could not be located as reported earlier [37]. Optimized geometries of the transition states of both modes [S & A] and their activation parameters



Scheme-I: [1,5]-Shift in benzene annealed 1,3-pentadiene analogues where X = H (**I**); X = F (**II**); X = Cl (**III**); X = Br (**IV**); **A =** Benzene ring



Scheme-II: [1,5]-shift in naphthalene annealed 1,3-pentadiene analogues where X = H (**V**); X = F (**VI**); X = Cl (**VII**); X = Br (**VIII**); **B** = Ring 1; **C** = Ring 2

($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ & $\Delta S^{\ddagger}$) have been presented in Figs. 1 & 2 respectively. According to W-H rule suprafacial [1,5]-shift is thermally allowed and antarafacial [1,5]-shift is forbidden, but fluorine shift tends to follow antarafacial pathway (contra W-H) [37]. In the present paper, our focus lies on the effect of annealed benzene/(or) naphthalene ring in deciding the stereochemical pathways of the [1,5]-shift of X in the systems under study. Table-1 showed that benzene and naphthalene ring annealed to pentadiene making it an embedded diene have commensurately increased the barrier of both the stereochemical modes supra and antara relative to the simple 1,3-pentadiene [37] (Table-1).

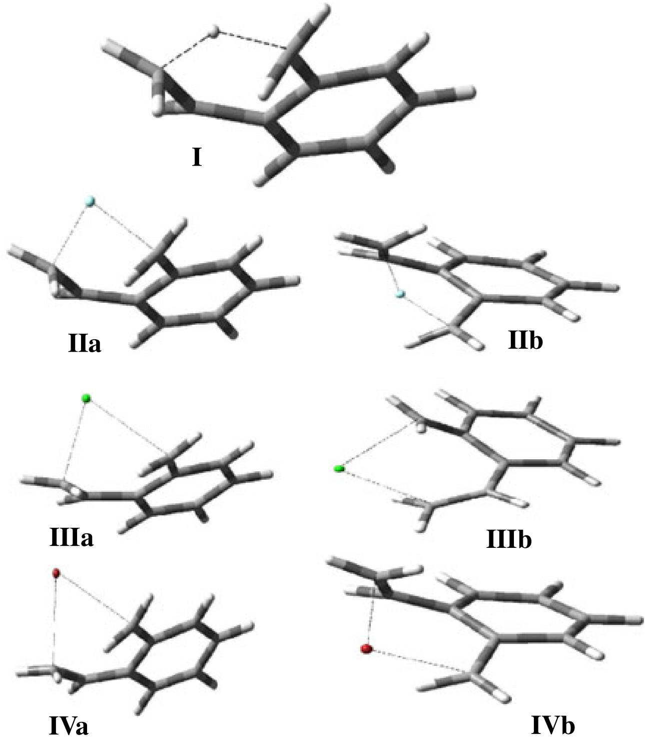


Fig. 1. Optimized geometries of transition states (TSs) of benzene annealed 1,3-pentadiene and its halogen analogues at B3LYP/6-31G(d,p) level where H = **I**; F = **II**; Cl = **III**; Br = **IV**, STS: **IIa**, **IIIa** & **IVa**; ATS: **IIb**, **IIIb** & **IVb**

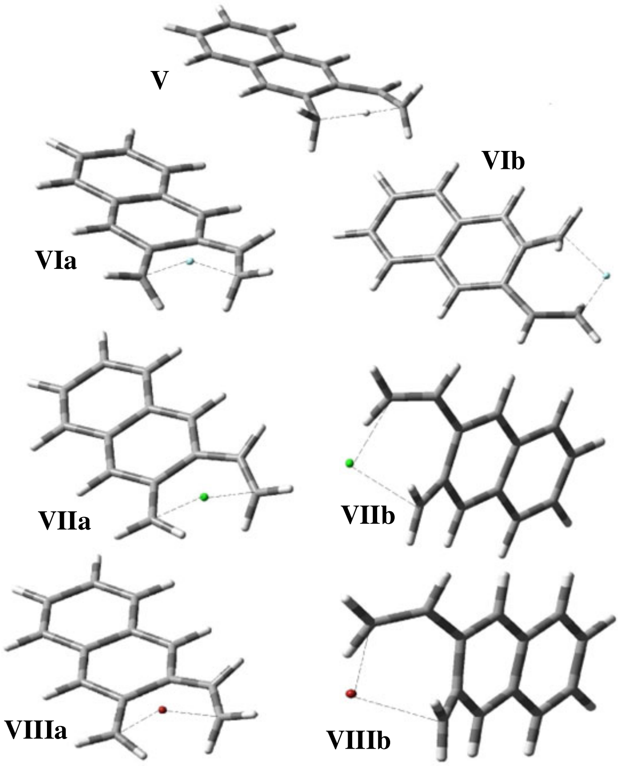


Fig. 2. Optimized geometries of transition states (TSs) of naphthalene annealed 1,3-pentadiene and its halogen analogues at B3LYP/6-31G(d,p) level where H = **V**; F = **VI**; Cl = **VII**; Br = **VIII**, STS: **VI(a)**, **VII(a)** & **VIII(a)**; ATS: **VI(b)**, **VII(b)** & **VIII(b)**

The benz and naphtha fused systems each show an increase of about 10 & 15 kcal/mol, respectively in their [1,5]-X shift barrier than free 1,3-pentadiene. As there is an increase in barrier on benzene ring and naphthalene ring fusing, it could be looked up as an additive effect due to benzene ring. This increase in barrier might be due to alternation/loss of aromaticity in the benzene ring in the reaction coordinate or due to other electronic phenomenon.

Does fused benzene/naphthalene ring alter the preference of fluorine shift from the contra Hoffman antarafacial mode

TABLE-1
ACTIVATION PARAMETERS OF THE [1,5]-X SHIFT IN SYSTEMS **I-VIII** CALCULATED AT B3LYP/6-31G(d,p) LEVEL

System	[1,5]-Suprafacial mode				[1,5]-Antarafacial mode				$\Delta\Delta G^{\ddagger}_{S\text{-}A}$* (kcal/mol)
	$\Delta E^{\ddagger}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K/mol)	$\Delta E^{\ddagger}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K/mol)	
I	42.58	41.88	43.90	6.77	–	–	–	–	–
	32.17	*31.32*	*33.20*	*6.30*					
II	67.90	67.58	68.53	3.19	57.16	56.87	57.72	2.88	10.81
	57.56	*57.17*	*58.28*	*3.7*	*47.50*	*47.08*	*48.23*	*3.8*	*10.05*
III	40.67	40.44	41.09	2.18	45.07	45.04	45.06	0.06	-3.97
	30.36	*29.95*	*31.29*	*4.5*	*37.64*	*37.43*	*38.18*	*2.5*	*-6.89*
VI	35.31	35.01	35.78	2.58	43.37	43.31	43.29	-0.06	-7.51
	24.55	*24.17*	*25.22*	*3.6*	*35.55*	*35.4*	*36.19*	*2.6*	*-10.96*
V	47.77	47.11	48.98	6.29	–	–	–	–	–
VI	71.85	71.56	72.45	2.99	61.35	61.10	61.87	2.57	10.58
VII	44.82	44.77	44.70	-0.25	47.26	47.26	47.25	-0.05	-2.55
VIII	40.39	40.16	40.67	1.73	45.99	45.96	45.94	-0.05	-5.27

*$\Delta\Delta G^{\ddagger}_{S\text{-}A}$ refers to free energy between suprafacial TS and antarafacial TS.
Values in italic represent the activation parameters of [1,5]-X shift in 1,3-pentadiene

TABLE-2
AROMATICITY INDICES COMPUTED FOR THE TRANSITION STATES (TSs) OF **I** TO **VIII**

System	[1,5]-Suprafacial mode		[1,5]-Antarafacial mode		ΔNICS(0)*	ΔNICS(1)*
	NICS(0)	NICS(1)	NICS(0)	NICS(1)		
I	-13.68	-6.13	–	–		
		-14.03	–	–		
II	11.4	7.24	-7.41	-7.11	18.81	14.35
		7.62		*-6.11*		*13.73*
III	-0.98	-4.58	9.68	6.2	-10.66	-10.78
		-0.98		*7.75*		*-8.73*
IV	-3.18	-6.42	13.43	10.05	-16.61	-16.47
		-3.18		*11.23*		*-14.41*
V	-5.4	-7.37	–	–		
		-1	–	–		
VI	13.03	10.71	-7.97	-6.66	21	17.37
		8.41		*-7.53*		*15.94*
VII	-1.99	-5.38	11.76	12.15	-13.75	-17.52
		-2.09		*5.02*		*-7.11*
VIII	-2.76	-7.32	15.79	15.48	-18.55	-22.79
		-2.03		*10.25*		*-12.28*

*ΔNICS refers to the difference between corresponding suprafacial and antarafacial modes. Values in italic refer to NICS 1Å above the plane.

to Hoffmann allowed suprafacial mode? Does the ring fusing bring any change in the preference of suprafacial shift of chlorine /bromine? Table-1 reveals the following: The BP(F) & NP(F) tends to choose only antara mode while BP(H, Cl & Br) choose supra mode for [1,5]-X shift. The barrier trend is as follow: NP/BP(Br)$_{supra}$ < BP(Cl)$_{supra}$ < BP(H)$_{supra}$ < BP(F)$_{antara}$. This trend is exactly similar to 1,3-pentadienes. Further, the $\Delta\Delta G^{\ddagger}_{S\text{-}A}$ remains the same for X = F, but it decreases for (X = Br, Cl) in both BP and NP systems implying that antarafacial is becoming more facile.

Role of aromaticity in the rate and stereochemistry of the reaction: Nucleus Independent Chemical Shift (NICS) values in Table-2 indicates the aromaticity of the sigmatropic transition states at benzene/naphthalene ring centres. The aromaticity of suprafacial TS are more aromatic (characterized by a more negative NICS value) while antarafacial modes are antiaromatic (positive NICS values) in the case of H, Cl & Br shifts. But fluorine shift is opposite; TS of supra mode is antiaromatic (positive NICS) and antara mode is aromatic (negative NICS). This is consistent to earlier report [37] favouring the Contra Hoffmann [1,5]-F shift *via* antarafacial mode. Further, the fact that aromaticity of TS decides the favouredness of the pathway has been established by relatively excellent correlation (Table-3) (0.9) between ΔNICS(0,1) and (supra-antara) $\Delta\Delta G^{\ddagger}_{S\text{-}A}$ of BP(X) & NP(X) systems (Fig. 3). Now let us focus on the aspect of aromaticity loss of benzene and naphthalene ring at the TS as the factor behind increase in reaction barrier. Table-4 lists the loss of aromaticity in benzene ring (**A**) of BP systems and ring 1 & 2 of naphthalene rings (**B** & **C**) of NP systems relative to their reactants. To envisage the direct effect of loss of aromaticity correlation between ΔΔNICS(0,1) & $\Delta\Delta G^{\ddagger}_{S\text{-}A}$ of benz and naphtha systems (Table-5) is done. A relatively good correlation establishes our assumption that enhancement in barrier is due to loss of aromaticity in the fused rings (Fig. 4).

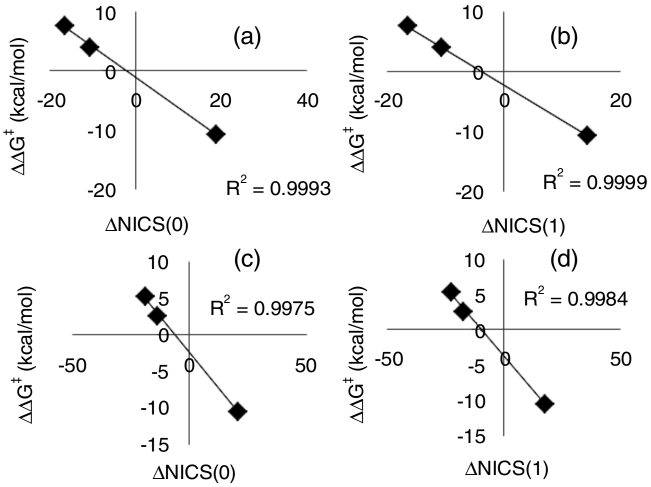


Fig. 3. Correlation between $\Delta\Delta G^{\ddagger}_{S\text{-}A}$ and ΔNICS of TSs [(a) & (b) Correlation plots for BP(X); (c) & (d) Correlation plots for NP(X)]

TABLE-3
CORRELATION COEFFICIENT OF AROMATICITY INDEX ΔNICS of TSs WITH $\Delta\Delta G^{\ddagger}_{S\text{-}A}$

Parameter	ΔNICS(0)	ΔNICS(1)
(BP(X)) $\Delta\Delta G^{\ddagger}$	0.9993	0.9999
(NP(X)) $\Delta\Delta G^{\ddagger}$	0.9975	0.9984

Conclusion

[3,4]-Benz and naphtha fused 1,3-pentadiene undergo [1,5]-shift of H/F/Cl/Br relatively slower than their 1,3-pentadiene analogue. But the preference of contra Woodward-Hoffmann antarafacial stereochemical pathway for [1,5]-fluorine shift repeats back. However, other halogens favour [1,5]-suprafacial shift. Although stereochemical pathway has not been altered upon ring fusing, they have enhanced the barriers, which commensurately correlates with loss of aromaticity of benzene and naphthalene ring at the TS measured in terms of as NICS. Hence, this article adds up to the fact that aromaticity of TS goes hand in hand with the aromaticity of residual ring in determining the path and rate of the reaction.

TABLE-4
AROMATICITY INDICES OF RINGS (**A**, **B** AND **C**) IN THE TSs OF **I** TO **VIII**

System	[1,5]-Supra mode		[1,5]-Antara mode		Supra-antara		$\Delta\Delta G^{\ddagger}_{S\text{-}A}$
	ΔNICS(0)[1]	ΔNICS(1)[1]	ΔNICS(0)[1]	ΔNICS(1)[1]	ΔΔNICS(0)	ΔΔNICS(1)	
A (BP(X))							
I	-1.52	-1.15	–	–	–	–	–
II	-10.16	-9.09	-3.24	-2.91	-6.92	-6.18	10.81
III	-5.84	-4.97	-10.11	-7.06	4.27	2.09	-3.97
IV	-4.4	-3.59	-4.22	-3.8	-0.18	0.21	-7.51
B (NP(X))							
V	-0.22	-1.24	–	–	–	–	–
VI	-12.62	-10.87	-5.22	-1.78	-7.4	-9.09	10.58
VII	-5.39	-3.34	-9.03	-10.1	3.64	6.76	-2.55
VIII	-4.63	-3.32	-12.14	-13.64	7.51	10.32	-5.27
C (NP(X))							
V	-2.33	-1.78	–	–	–	–	–
VI	-8.99	-7.63	-3.09	-2.8	-5.9	-4.83	10.58
VII	-5.23	-4.06	-7.8	-6.44	2.57	2.38	-2.55
VIII	-5.8	-4.74	-9.99	-8.26	4.19	3.52	-5.27

[1] ΔNICS(0,1) values represent the difference in NICS(0,1) values between reactants and their corresponding TSs.

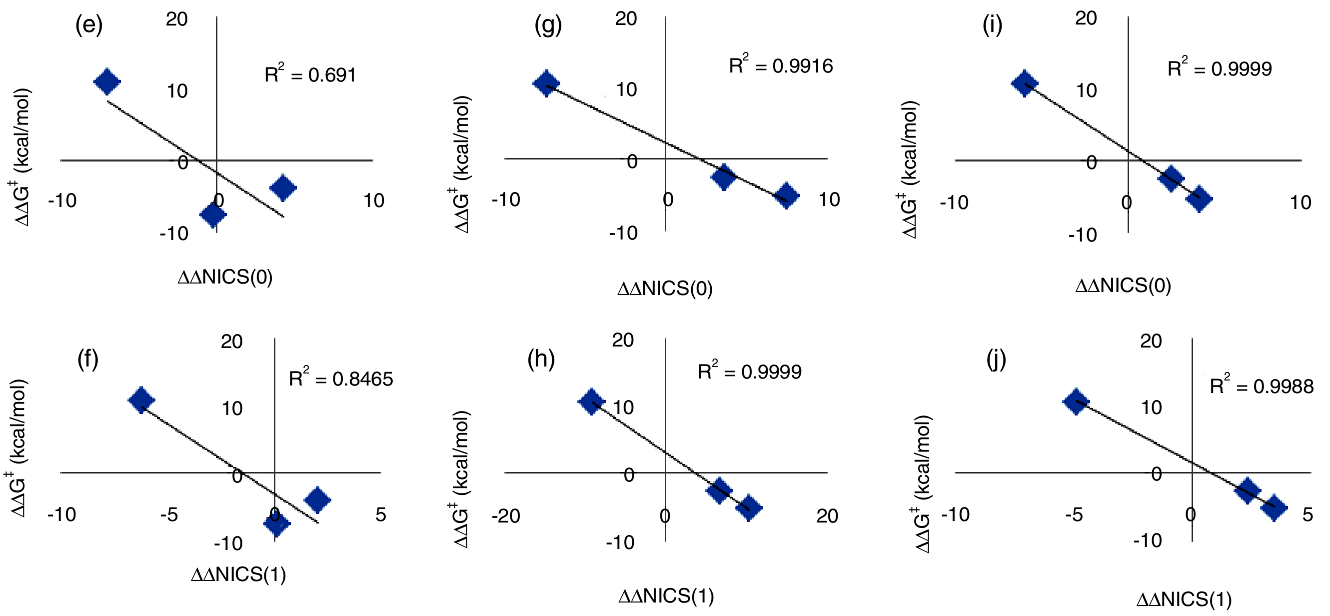


Fig. 4. Correlation between $\Delta\Delta G^{\ddagger}_{S\text{-}A}$ and ΔΔNICS of rings (**A**, **B** & **C**) [(e) & (f) Correlation plots for **A** in BP(X); (g) & (h) Correlation plots for **B** in NP(X); (i) & (j) Correlation plots for **C** in NP(X)]

TABLE-5
CORRELATION COEFFICIENT OF AROMATICITY INDEX ΔΔNICS OF RINGS WITH $\Delta\Delta G^{\ddagger}_{S\text{-}A}$

System	ΔΔNICS(0)[2]	ΔΔNICS(1)[2]
A $\Delta\Delta G^{\ddagger}$	0.691	0.8465
B $\Delta\Delta G^{\ddagger}$	0.9916	0.9999
C $\Delta\Delta G^{\ddagger}$	0.9999	0.9988

[2] ΔΔNICS(0,1) values represent the difference in ΔNICS(0,1) values between suprafacial and antarafacial modes.

ACKNOWLEDGEMENTS

One of the authors, LA thanks Dr. P. Venuvanalingam, Emeritus Prof. School of Chemistry, Bharathidasan University, for his support and the University Grants Commission, New Delhi, India for the financial assistance through minor research project (No. F-MRP6409/16(SERO/UGC)).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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