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A computational study of aromaticity-controlled Diels–Alder reactions

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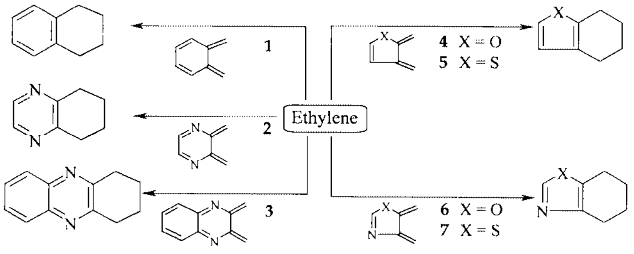
The prime role of aromaticity in Diels–Alder reactions is studied computationally by *ab initio* and DFT methods using various masked dienes and ethylene. The reactions under consideration yield both aromatic stabilized and destabilized products through a concerted transition state due to the effect of ring functions embedded in the diene framework. Computations reveal that the cycloadditions involving various quinodimethanes achieve a progressive aromaticity gain during the reaction by the influence of aromatic functionalization; therefore they are kinetically as well as thermodynamically much more favorable than the typical butadiene–ethylene reaction. A series of these reactions affirms that the degree of aromatization increases with decreasing barrier and increasing exothermicity of a reaction. In reactions of benzo[*c*]heterocycles, aromaticity is lost due to the reacting heterocycle, but is gained by the adjacent hexagon during the reaction course. A partly occurring aromatic stabilization process in these reactions seems to facilitate the cycloaddition, but the remaining aromatic destabilization decreases the reaction rate and energy as compared to quinodimethane reactions. In the reactions of polyaromatic hydrocarbons *viz.* styrene, anthracene and pentacene, only loss of aromaticity occurs by virtue of aromatic defunctionalization. The progress of aromatization as well as dearomatization is evidenced from the nucleus independent chemical shifts (NICS) values whereas the aromaticity of the transition state and product is quantified by magnetic susceptibility exaltation (MSE) calculations. Calculations thus establish with both magnetic and energetic criteria that the aromatic stabilization process as well as the aromatic ring function of the masked diene accelerates the reaction to the maximum extent through an ‘early’ TS, but the aromatic destabilization deactivates the cycloaddition *via* a ‘late’ TS.

Introduction

The Diels–Alder reaction[1] is the most prominent representative of cycloadditions used for various organic synthesis and its mechanism[2] is now clearly understood.[3,4] The preparative use of these reactions has been greatly increased by the development of new kinds of dienes and dienophiles. The wide variety of these reactants has highlighted various factors determining the mechanism of these reactions. Masked dienes and dienophiles—the reacting function is covered either internally or externally by a ring or cage-like framework—are often introduced in Diels–Alder reactions.[1] As both reactants show their hidden functionality, the normal changes occurring in the reacting functions alter the remaining function. These changes might be a significant factor by which to judge the feasibility of a reaction. The aromatization and dearomatization in the reactions involving this class of dienes and dienophiles are well known examples. Quinodimethanes[5–7] and *o*-benzynes[1b,c,2c,8] act as dienes and dienophiles respectively and form aromatic stabilized adducts while the reactions of aromatic dienes, five-membered heterocycles,[1c] anthracene,[2c,9] pentacene,[10] styrene[2c,11] *etc.* and fullerene[12] dienophiles produce aromatic destabilized products. The influence of aromatic stabilization and destabilization appears to determine the reaction energy path, but a detailed understanding of this aspect is still lacking, although enormous experimental[5–12] and theoretical[13,14] studies of these reactions are available. This stimulated us to probe theoretically certain Diels–Alder reactions of this kind to explore aromaticity[15] as the only factor to be fully responsible for the reaction.

The investigation is confined to some selected masked dienes from numerous known systems and ethylene as the dienophile.



Scheme 1

The reactions **1**–**7** (Scheme 1) involving outer–outer ring dienes *viz. o*-quinodimethane[5] (A), pyrazinoquinodimethane[7g,h] (B), quinoxalinoquinodimethane[7e] (C), furanoquinodimethane[7f,h] (D), thiophenoquinodimethane[7f] (E), oxazolinoquinodimethane[7f] (F) and thiazolinoquinodimethane[7f] (G) are chosen to study the role of aromatic stabilization in the reaction barrier. Herein, the relative preference of various aromatization processes is systematically analyzed based on the quantified aromaticity and energetics. When we deal with the aromatization of heterocyclic analogs (reactions **4**–**7**), the dearomatization occurring in the reactions of similar heterocycles[13] is studied in parallel with a view to judging the equal aromaticity gain and loss. In order to predict the interplay of aromaticity between the two rings, the benzene fused five-membered ring compounds, namely benzo[*c*]cyclopentadiene[16] (H) or indene, benzo[*c*]furan[17] (I) and benzo[*c*]thiophene[18] (J), are selected for the reactions (**8**–**10**) depicted in Scheme 2. The aromatic destabilization in the reaction of polyaromatic hydrocarbons is another point of interest. Therefore, the reactions **11** and **12** (Scheme 2) involving 1-vinylnaphthalene[2c,11] (K) and anthracene[2c,9] (L)—

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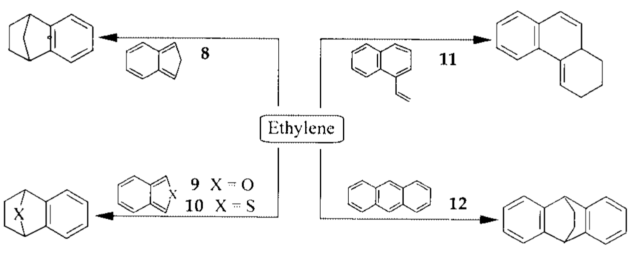


Scheme 2

the reaction proceeds *via* an inner–outer and inner–inner ring diene respectively in both cases—are employed to show the effect of mere aromaticity loss on the reaction profile. Subsequently, the influence of an extra aromatic ring function along the barrier is further tested using the pentacene[10] (M) reaction. This report is a sequel to our work on the "dual-aromaticity" aspect which was introduced for the transition structure (TS) of quinodimethane reactions[19] recently.

The transition state geometry of Diels–Alder[20a] and other pericyclic reactions[20b] has been recognized as a delocalized aromatic ring for a long time and this has been confirmed by recent computations on NMR related properties.[21] In the present set of reactions, the six-electron cyclic delocalization[21g] in the TS will be accompanied by a stabilized/destabilized π-delocalization of the adjacent ring and their net aromaticity would have a great influence on the reaction barrier. The aromatic behavior of the ground and TS geometries is assessed from magnetic susceptibility exaltation[22] (MSE) and Schleyer's nucleus independent chemical shift[23] (NICS) criteria.

Computational details

Computations for a comprehensive set of Diels–Alder reactions (**1**–**12**) were performed by both *ab initio*[24] and density functional theory (DFT) methods using the GAUSSIAN 94 program.[25] The stationary point geometries were fully optimized at HF as well as B3LYP[26] levels with the 6-31G* basis set.[24] The B3LYP functional has been used successfully in our own group for reaction path following as shown by a collection of recent reports[27] and related studies on both conceptual and computational aspects of DFT.[28–31] Force calculations were done to examine the occurrence of a single imaginary frequency for the TS. To evaluate the energetics, single point calculations were performed including diffuse functions at the B3LYP/6-311+G** level on a B3LYP/6-31G* structure. The magnetic susceptibilities and the diamagnetic shieldings were calculated respectively by CSGT[32] and GIAO[33] methods with a 6-311+G** basis set[24] on a B3LYP/6-31G* geometry to acquire the MSE and NICS values. In view of the large number of atoms involved in the pentacene reaction, the optimizations were carried out at the B3LYP level with the 3-21G basis set[24] and the related results are compared with the anthracene reaction at the same level. The magnetic susceptibility exaltation in the TS (Λ_{TS}) and product (Λ_P) is calculated by taking the reactants as reference systems[20] and their net amount decides the aromaticity of the whole system.

Results and discussion

Aromatization in quinodimethane reactions

The quinodimethane reactions (**1**–**7**) produce various aromatized cycloadducts which are the derivatives of benzene, pyrazine, quinoxaline, furan, thiophene, oxazole and thiazole. The fused ring function in A, B and C is symmetric in nature while the rest of the quinodimethanes (D, E, F and G) have unsymmetrical ring functions. In light of this, the former dienes react through the synchronous TSs (**TS1**–**TS3**) whereas the latter cases show the asynchronous TSs (**TS4**–**TS7**) drawn in Fig. 1. Owing to the aromatization process, the two new σ-bonds (**d** and **f**, Fig. 2) seem to be formed quickly whilst the dienophile π-bond (**e**) is cleaved quickly in the TSs of the title reactions (**TS1**–**TS7**) compared to the TS of the prototype reaction between butadiene and ethylene (**TSI**), because the σ-bonds are found to be much weaker[34] and the π-bond is stronger[34] in the former TSs than in the latter TS as seen from the bond distances. The higher bond alternation (Fig. 1) found for **TS1** through **TS7** in comparison with **TSI** implies a greater degree of bond maturation. Collectively, these bond criteria reveal that the reactions **1**–**7** proceed through "early" matured TSs in relation to the prototype case. The TSs studied here further show that the weakness of the formed σ-bonds (**d** and **f**), and the bond alternation in the **a**, **b** and **c** bonds is increased, whereas the cleaved π-bond (**e**) strength is decreased, in the order: **TS3** > **TS1** > **TS2** > **TS5** > **TS7** > **TS4** > **TS6** as can be noticed from Fig. 1. The "early"/"late" type of the TS can thus be recognized from this trend.

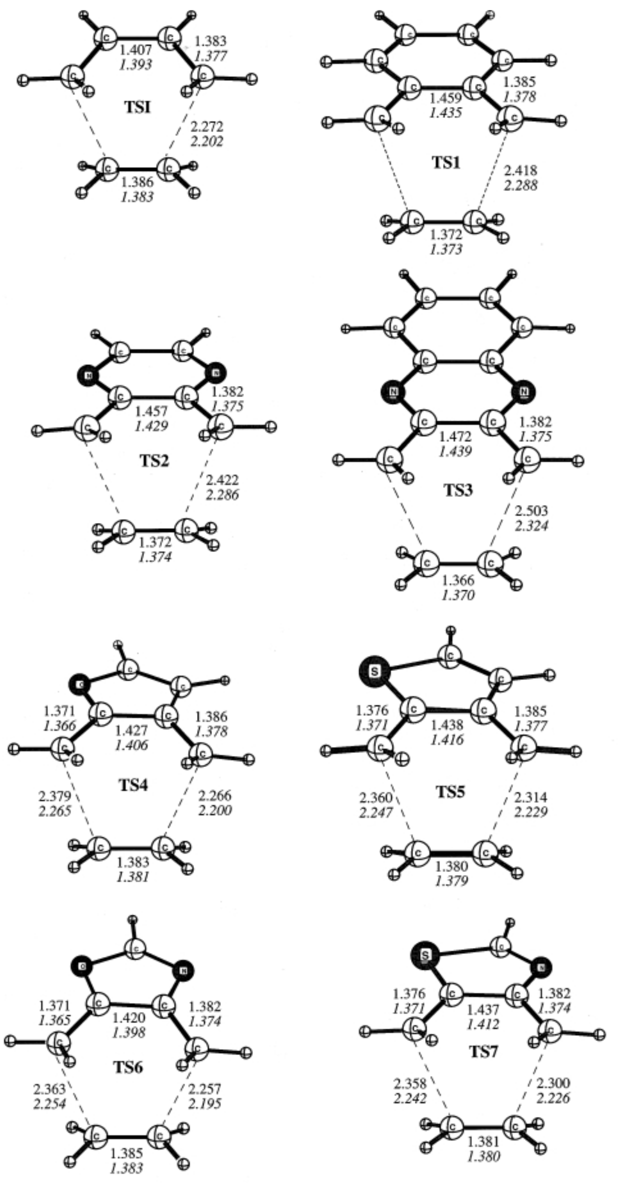


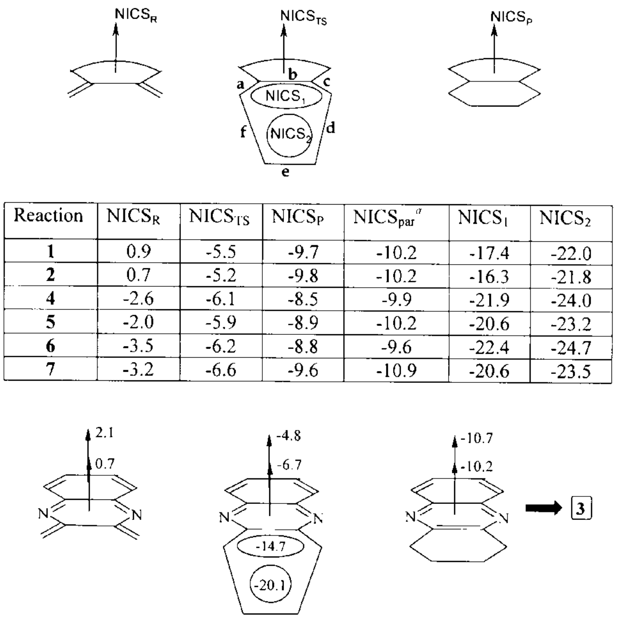
Fig. 1 Computed TSs of the Diels–Alder reactions involving various quinodimethanes and ethylene (**TS1** to **TS7**) with selected geometric parameters (Å). The **TSI** of the butadiene–ethylene reaction is shown for comparison. The B3LYP/6-31G* and HF/6-31G* values are respectively given in normal type and italics.

The π-bond generation in the diene unit during reaction assists the aromatization or "aromatic functionalization" process and the aromaticity on the fused diene ring is thereby progressively increased from reactant to product *via* the TS as

Table 1 Computed activation and reaction energies (kcal mol^{-1}) of the Diels–Alder reactions involving various quinodimethanes (**1**–**7**) and the MSE of TS and product (ppm, cgs)

	$\Delta E^{\ddagger}$				ΔE_r			
Reaction	i[a]	ii[a]	iii[b]	Λ_{TS}	i	ii	iii	Λ_P
I[c]	45.0	22.4	25.4	−19.8	−42.9	−43.1	−35.7	−4.9
1	29.6	8.5	11.0	−30.7	−72.3	−70.9	−63.5	−21.4
2	29.3	7.7	10.0	−29.4	−73.2	−72.3	−65.8	−21.0
3	26.0	4.5	6.7	−41.4	−86.0	−82.8	−76.0	−39.2
4	38.7	15.6	18.4	−24.6	−54.1	−54.7	−47.4	−11.1
5	35.8	13.7	16.3	−25.4	−57.4	−57.7	−50.7	−14.5
6	39.8	16.5	19.2	−24.0	−52.1	−53.0	−46.0	−10.3
7	36.2	14.0	16.6	−24.4	−57.0	−57.2	−50.5	−13.8

[a] Optimizations at HF/6-31G* (i) as well as at B3LYP/6-31G* (ii) levels. [b] The single-point calculations at B3LYP/6-311+G** (iii) on B3LYP/6-31G* geometry. [c] The prototype reaction involving butadiene and ethylene.



Reaction	NICS$_R$	NICS$_{TS}$	NICS$_P$	NICS$_{par}$[a]	NICS$_1$	NICS$_2$
1	0.9	-5.5	-9.7	-10.2	-17.4	-22.0
2	0.7	-5.2	-9.8	-10.2	-16.3	-21.8
4	-2.6	-6.1	-8.5	-9.9	-21.9	-24.0
5	-2.0	-5.9	-8.9	-10.2	-20.6	-23.2
6	-3.5	-6.2	-8.8	-9.6	-22.4	-24.7
7	-3.2	-6.6	-9.6	-10.9	-20.6	-23.5

Fig. 2 Schematic representation of the NICS approaches in reactant, TS and product of reactions **1**–**7** defining NICS$_R$, NICS$_{TS}$ and NICS$_P$, calculated 1 Å above the center of the outer ring in the respective geometries. The in-plane aromaticity of the TS is defined based on two different planes providing NICS$_1$ and NICS$_2$ respectively. The case of F involving two aromatic ring functionalizations is shown in a separate scheme. [a] The NICS calculated at the ring of the parent system (benzene, pyrazine, quinoxaline, furan, thiophene, oxazole and thiazole).

revealed by NICS$_R$, NICS$_{TS}$ and NICS$_P$ (Fig. 2). The ring functions of the TS and product achieve around 50% and 100% aromaticity respectively with respect to the related parent systems (NICS$_{par}$). On the other hand, the reactions proceed *via* a σ,π-cyclic delocalized TS since all carbons are rehybridized roughly from sp^2 to $sp^{2.5}$ during the bond make–break process, but this delocalization will be totally lost in the product. Obviously, both NICS$_1$ and NICS$_2$ (Fig. 2) show large diatropic shifts, ranging from −16.3 to −24.7 ppm, in the TS, predicting the aromatic behavior of the cyclic TS mimicking benzene.[23] C is a benzene-fused pyrazine derivative and so this involves two π-delocalizations in the reaction as shown by the NICSs in Fig. 2. Its aromatization would still have a greater impact on the barrier than in other cases. Though the NICSs specify the individual aromatic character of these delocalizations, the net aromaticity of the TS and product can apparently be quantified from the MSE criterion.

The resonance stabilized TS and product of these reactions are highly aromatic compared to the butadiene–ethylene reaction. Evidently, both Λ_{TS} (−24.0 to −41.4 ppm, cgs range) and Λ_P (−10.3 to −39.2 ppm, cgs range) in the former reactions are appreciably larger than those found in the latter (−19.8 and −4.9 ppm, cgs). This is the reason why these TSs are formed earlier than a typical TS as demonstrated by the bond criteria. Consequently, the quinodimethane reactions (**1**–**7**) are extremely fast and are exothermically very favorable in relation to the prototype reaction as can be seen from the reaction energetics (Table 1). The MSEs further reveal that the extent of aromatization in the TS and product decreases along the reaction series: **3** > **1** > **2** > **5** > **7** > **4** > **6** as both Λ_{TS} and Λ_P values (Table 1) show a decrease in magnitude in this order, which also parallels the aromaticity trend[15b,c] in the concerned isolated rings. As could be expected, this is consistent with the trend in "earliness" of TS as predicted on the basis of bond parameters. Calculated activation and reaction energies show that the reaction rate and the exothermicity also decrease in the same manner. This is in accordance with the Hammond postulate.[35] Thus, it broadly emphasizes the fact that the aromaticity gain in the reaction greatly enhances the reaction efficiency and hence all quinodimethane reactions[5–7] are performed *in situ*. As expected, the two π-aromatizations in reaction **3** accomplish the most aromatic TS and product due to the largest MSE value as compared to the single aromatization in the other reactions. Therefore, reaction **3** is much more favorable than the remaining reactions (**1**–**6**) as shown by the relative energies. The degree of aromatization in reactions **1** and **2** seems to be greater compared to the reactions **4**–**7** as revealed by Λ_{TS} and Λ_P values. This is indeed in line with the more aromatic character[15b,c] of benzene and pyrazine as compared to the five-membered heterocycles (furan, thiophene, oxazole and thiazole). The reactions **1** and **2** are therefore significantly faster and more exothermically favorable than the reactions **4**–**7**. The TS and product of **1**, analogous to benzene, are expected to be slightly more aromatic than the pyrazine analogues of **2** as shown by MSEs (Table 1), but reaction **1** is slightly less favorable than **2** as seen from the reaction energetics. This can be due to the fact that the electron-donating ability of the nitrogens *via* their σ-lone pair in B overwhelms the influence of aromaticity. Calculated MSEs predict that the aromaticity gain in **4**–**7** is almost similar. However, the TS and product of heterocyclic analogs maintain their aromaticity trend as found in the parent systems.[15b,c] Therefore, the activation and reaction energies (Table 1) of these reactions are also in the same order based on a high degree of aromatization. The thiophene and thiazole analogues are expected to be more aromatic than the furan and oxazole derivatives respectively as predicted by Λ_{TS} and Λ_P. The reactions **5** and **7** thus cause a smaller barrier and more exothermicity relative to **4** and **6**. It is worth highlighting the fact that the aromaticity is equally lost in the TS and product—the more aromatic reactant loses its aromaticity to the maximum extent during reaction—when the similar aromatic heterocycles serve as dienes in the reaction (Fig. 3) and this can be seen from the MSE values. Therefore, the relative aromaticity loss parallels the trend in barrier and exothermicity as can be seen from the energetics (Fig. 3). It is clearly understood from the results

X	Λ_R	$\Delta E^\ddagger$	Λ_{TS}	ΔE_r	Λ_P
O	-8.9	25.0	-12.3	-8.5	-0.5
S	-13.0	34.1	-9.7	-6.3	4.7

X	$\Lambda_R{}^a$	$\Delta E^\ddagger$	Λ_{TS}	ΔE_r	Λ_P
O	-8.7	23.4	-11.9	-10.5	-0.2
S	-12.3	30.9	-9.4	-9.5	3.0

Fig. 3 Diels–Alder reactions involving the aromatic heterocycles as dienes, their activation and reaction energies (kcal mol^{-1}) and related MSEs (Λ_{TS} and Λ_{TS}, ppm, cgs).

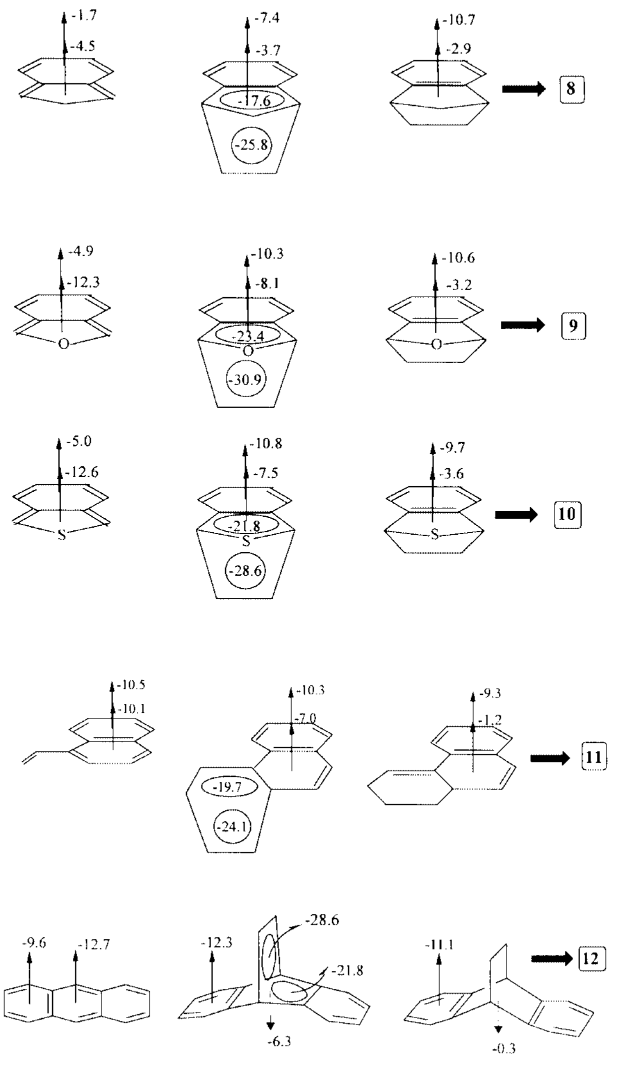


Fig. 4 NICS values calculated over various rings of reactant, TS and product geometries involved in the reactions **8** to **12** as described in Fig. 2.

that the amount of aromaticity loss found in the reactions depicted in Fig. 3 is gained by the reactions **4**–**7** to almost the same extent.

Aromatization and dearomatization in the reactions of benzo[*c*]cycles

The benzene fused five-membered cyclic compounds *viz.*, H, I and J form benzo bicyclic adducts (Scheme 2) concertedly by securing synchronous TSs (**TS8**, **TS9** and **TS10**) shown in Fig. 5 as the reactions take place at their symmetric five-membered rings.[16–18] The formed bonds (**b**, **d** and **f**) are strengthening while the cleaved bonds (**a**, **c** and **e**) are weakening in the TS series leading to a "late" maturation of the TS as evidenced from the bond distances.[33] The reacting heterocyclic functions of H and I are relatively more aromatic[36] than the adjacent hexagonal ring as revealed by NICS (Fig. 4). Hence, the former function progressively loses its aromaticity in the reaction by the disruption of the π-delocalization whereas the latter function subsequently gains a ring current through the π-bond maturation as can be noticed from the NICSs. Moreover, the reacting cyclopentadiene unit of H is expected to be non-aromatic, but its peripheral ring gains aromaticity during the reaction. The NICS indices (Fig. 4) clearly indicate this effect. The cycloadduct framework of all TSs shows their usual σ,π-delocalization through the large NICS magnitudes.

Although the aromatization of these reactions is quite similar to the quinodimethane cycloadditions, the present reactions are distinct from the previous cases by the dearomatization of the reacting ring function. The aromaticity indicator, MSE, thus shows that the aromatic behavior of the TS and product in the reactions **8**–**10** is considerably reduced as compared to those species occurring in **1**. Between I and J, the reacting thiophene ring of the latter system is known to be more aromatic[36] than the furan function of the former case and this is also supported by the NICS values (Fig. 4). In fact, their aromaticity is equally lost along with the π-aromatization in **9** and **10**; the former reaction thus produces the less aromatic TS and product compared to the latter one as predicted by both Λ_{TS} and Λ_P (Table 2). This is already realized by the complete aromaticity loss in the reactions of simple aromatic heterocycles (Fig. 3). Therefore, reaction **9** is appreciably faster and more exothermic than **10** as shown by the energetics. Although the aromatization process accelerates the reactions to some extent, the aromaticity loss occurring in the reactions opposes this effect. This is proven by the relative energies (Table 2) through the quantified aromaticity (MSE values). Similar energy trends have been reported in the literature at the AM1 level.[14b,e] Specifically, reaction **10** faces a heavy loss in aromaticity that leads to a less favorable path even when compared with the typical reaction (**I**). The non-aromatic reacting function of H doesn't show any aromaticity loss. It can thus evolve to a more aromatic TS and product by only π-delocalization in reaction **8** as compared to **9** and **10**. Hence, the reaction of H with the dienophile is much facilitated over the others and this is clearly seen in the energetics of the reaction (Table 2). This section establishes that the aromatic destabilization becomes greater in the reaction series in association with the π-aromatization and so the reaction feasibility is found to decrease in the order: **8** > **9** > **10** as justified by both magnetic and energy criteria.

Dearomatization in the polyaromatic hydrocarbon reactions

The probable aromaticity of K and L is inferred from their individual rings in which the two rings of the first system have almost similar aromatic behavior while the central ring of the second case is more aromatic than the others. This is strongly supported by the NICS indices given in Fig. 4. It is essential to highlight the experimental fact that, upon reaction, K involves the diene function where it is only partly embedded in an aromatic ring while the reacting diene of L is fully embedded in the central ring. Accordingly, they go on to form their respective adducts, the phenanthrene derivative and ethanoanthracene, in a concerted manner[14a,i] through synchronous and asynchron-

Table 2 Calculated activation and reaction energies (kcal mol^{-1}) of the Diels–Alder reactions involving H (**8**), I (**9**), J (**10**), K (**11**) and L (**12**) along with the MSE of TS and product (ppm, cgs), calculation levels are identical to those in Table 1

	$\Delta E^{\ddagger}$				ΔE_r			
Reaction	i	ii	iii	Λ_{TS}	i	ii	iii	Λ_P
8	29.3	10.9	13.4	−23.3	−51.4	−48.8	−41.5	−15.5
9	31.4	15.4	18.0	−17.4	−36.9	−29.8	−24.3	−3.9
10	42.3	24.7	27.3	−12.5	−32.0	−27.1	−20.9	4.4
11	48.6	25.6	28.9	−15.7	−22.2	−20.3	−14.4	8.0
12	44.9	26.3	28.4	−11.9	−22.2	−19.5	−14.6	7.4

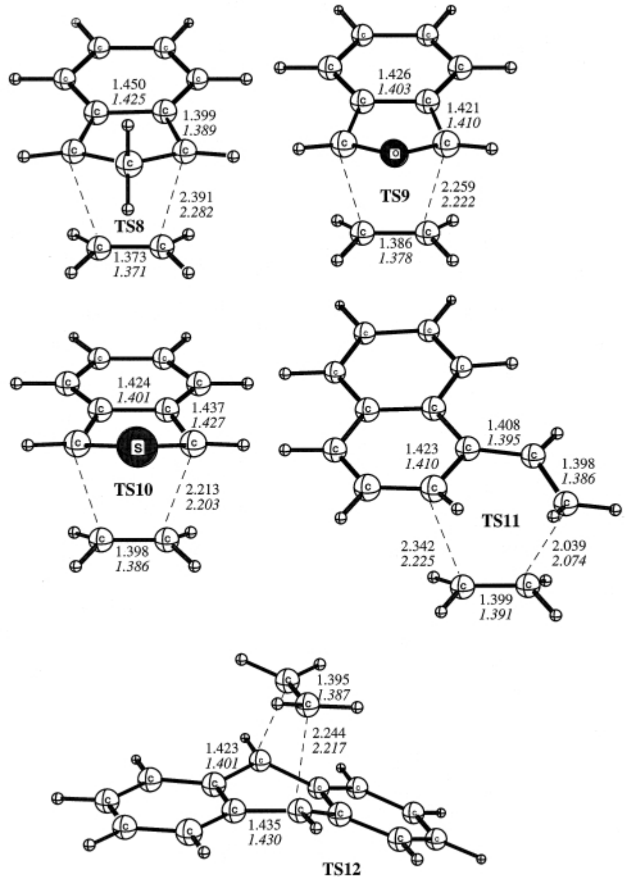


Fig. 5 Optimized TSs of the reactions of benzo[*c*]cyclopentadiene (**8**), benzo[*c*]furan (**9**), benzo[*c*]thiophene (**10**), 1-vinylnaphthalene (**11**) and anthracene (**12**) with ethylene and selected bond parameters (Å).

ous TSs (**TS11** and **TS12**) respectively shown in Fig. 5. The two reacting centers of vinylnaphthalene—the ring carbon and the terminal carbon of the vinyl group—are nucleophilically different and hence form differently matured new σ-bonds that illuminate the asynchronicity of **TS11**. It is decided by the bond criteria[34] that **TS11** is formed earlier than **TS12** since the formed and cleaved bonds of the former TS are matured to a greater degree as compared to the latter. The π-bond cleavage in the diene function—single cleavage in K cycloaddition and two cleavages in the L reaction—drastically reduces the aromaticity of the ring attached to the diene unit during reaction by the effect of resonance destabilization, but the aromaticity of the adjacent ring remains nearly the same as in the reactant. This can be clearly noticed from the NICS values (Fig. 4) illustrating the reaction progress. The cyclic delocalization of the TSs is understood from the in-plane aromaticity shown by the NICS.

The aromatic defunctionalization process of both reactions is realized from the aromaticity loss occurring in the ring associated with the diene which affects the net aromaticity of TS and product as predicted by the minimal values of Λ_{TS} and Λ_P (Table 2). This argument is a reminder of the conclusions of previous sections that the overwhelming effect of aromaticity in quinodimethane reactions (**1**–**8**) is highly marked by aromatization while in the reactions of benzo[*c*]heterocycles (**9**, **10**), it is only slightly pronounced due to π-delocalization rather than dearomatization. Therefore, the K and L reactions are kinetically as well as thermodynamically less favorable than the above reactions (**1**–**10**) as shown by the energetics (Tables 1 and 2). Indeed, the dearomatization process reduces the diene reactivity and exothermicity of the reaction while the aromatization increases them. Of the reactions **11** and **12**, the ring current is slightly disturbed in K during the reaction course and it is mostly affected in L. This is due to the position of the diene function fused to the ring. Based on this, **TS11** achieves greater aromaticity over **TS12**, as the Λ_{TS} values are found to be respectively −15.7 and −11.9, but their aromaticity is preserved by both cyclic delocalization and the adjacent ring. It is also evidenced from the relative aromaticity of the ring involved in the reactions **11** and **12**, in particular the highly aromatic central ring of L equally loses its aromaticity. Hence, the activation barrier of **11** should be higher than that of **12** and this is reproduced by the B3LYP/6-31G* calculation (Table 2). The positive magnitude of Λ_P signifies a complete aromaticity loss in the product and further predicts a similar aromaticity of the adducts of both reactions; the reactions thus proceed exothermically to the same extent as examined by the reaction energies. This happens because aromaticity is slightly gained by the adjacent ring of L during the product formation which is impossible for the K reaction. Though these reactions are relatively less efficient than the prototype reaction by dearomatization, the cycloadditions take place at a reasonable reaction rate because of the influence of neighboring aromatic ring functions. This is further supported by the reaction involving M in comparison with the reaction of L, because the former compound has two extra benzenoid rings over the latter. The reactions occur in the central rings of both polyaromatic systems which are apparently distinguished in the reaction path through the proximity effect; the excess of aromatic ring adjacent to the reacting ring in M remarkably enhances the reaction rate and exothermicity relative to L as revealed by the energetics (Table 3). The "early" nature of the TS in the former reaction denoted by the bond parameters[34] of **TS13** (Fig. 6) is further indicative evidence for this argument.

Table 3 The activation and reaction energies (kcal mol^{-1}) of the reactions involving L and M calculated at B3LYP/3-21G level

Reaction	$\Delta E^{\ddagger}$	ΔE_r
Anthracene + Ethylene	18.0	−31.5
Pentacene + Ethylene	13.3	−44.5

We finally mention that the activation barriers and reaction energies in the reaction series can be studied alternatively by a structure–activity relationship,[37] *e.g.* eqn. (1), where G_a

$$G_a = \Delta G + \lambda \ln[1 + \exp(-\Delta G/\lambda)] \qquad (1)$$

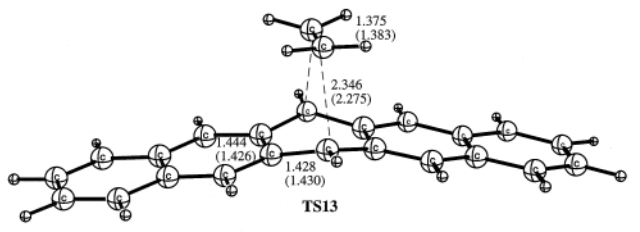


Fig. 6 The TS of the pentacene reaction optimized at B3LYP/3-21G with selected geometric parameters (Å). The values in parentheses denote the TS of the anthracene reaction.

represents the free energy of activation, ΔG the reaction free energy change and λ is a parameter constant for the reaction series. This equation was used in the past to study amongst others the reaction mechanism of gas phase Diels–Alder reactions,[38] but seemed less appropriate in the series considered in this paper because qualitative ideas on the influence of aromaticity on kinetics and energetics of these reactions are not exposed.

Conclusions

The present work reports high level computations on aromaticity-controlled Diels–Alder cycloadditions where several masked dienes react with ethylene. These reactions produce aromatic stabilized as well as destabilized adducts *via* a concerted mechanism by virtue of the functionalized ring attached to the diene unit. In quinodimethane cycloadditions, the ring function successively gains aromaticity along the reaction path due to aromatization. Hence, these reactions are indeed much faster and thermodynamically much more favorable than the prototype reaction involving butadiene–ethylene. Both aromatic stabilization and destabilization simultaneously exist in the reactions of benzo[*c*]heterocycles in which the reacting heterocycle completely loses its aromaticity while the adjacent hexagonal ring gains aromaticity during reaction. This opposing aromaticity effect moderately reduces both reaction rate and exothermicity—while part of the aromatization process enhances the reaction, the remaining dearomatization diminishes that effect—as compared to the previous set of reactions. The polyaromatic hydrocarbons such as vinylnaphthalene, anthracene and pentacene behave as dienes in cycloaddition; they reveal their unique aromaticity loss in the reaction course resulting in the least favorable reaction path among the reactions studied. However, it is the aromatic ring function fused to the diene unit which sufficiently controls the reaction. To conclude, the relative extent of aromatization and dearomatization of these reactions—the former process tremendously accelerates the reaction rather than the latter—is justified by the aromaticity of the resulting TS and product and their corresponding energies clarifying the decisive role of aromaticity in the reaction profile.

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