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Density functional theory study of the Diels–Alder reactivities of [*b*]-annelated cyclic five-membered dienes[†]

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epoc ABSTRACT: B3LYP/6–31G* calculcations were performed to model the Diels–Alder reaction of cyclobutano-, cyclobuteno- and benzo[*b*]- fused cyclic five-membered ring dienes with two prototypical dienophiles, ethylene and acetylene. The cyclobuteno[*b*]-fused dienes, which loose the unfavorable antiaromaticity upon cycloaddition, are the most reactive; in contrast, the benzo[*b*]-fused dienes, which encounter disruption of aromaticity in the course of the reaction, are the least reactive. Synchronicity calculations based on bond order analysis indicate that the reactions of benzo[*b*]-annelated dienes show significant deviations from synchronicity, indicating highly unsymmetrical transition states. Deformation energies were employed to corroborate the computed activation energies. Although there are some deviations in the quantitative results between ethylene and acetylene reactions, the trends are essentially the same with all the dienes considered, with acetylene showing a slightly higher reactivity. The comparison with the corresponding [*c*]-fused dienes further strengthens the argument that product stability controls the reactivity in these reactions, as exemplified by excellent linear fits between the activation and reaction energies. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: Diels–Alder reactions; density functional theory; masked dienes; activation energies; reaction energies; concerted mechanism; synchronicity; cycloadditions

INTRODUCTION

The Diels–Alder reaction is an elegant route to build novel polycyclic skeletons and is widely employed in several multiple-step syntheses of natural products.[1–4] The dienes can be broadly classified as simple, substituted and masked dienes. The masked dienes, which have been extensively studied experimentally[5–7] and theoretically,[8–12] can be categorized into cumulated, ring-fused and cage-fused dienes. The Diels–Alder reactions of simple five-membered heterocyclic ring dienes and their annelated analogues with a range of dienophiles lead to impressive Diels–Alder adducts,[8–11,13–16] and some of them have interesting industrial and biological applications.[1–3,17–20] The benzo-annelated five-membered rings have been the subjects of interest for several years and the experimental routes for both benzo[*b*]- and -[*c*]-annelated thiophenes and pyrroles have been known for some time, as these compounds are intermediates in the synthesis of biologically important species.[3,7,20,21] Jursic reported a semiempirical study on the cycloaddition reactions of benzo[*b*]- and benzo[*c*]-fused pyrrole, furan and thiophene with three dienophiles.[10] Manoharan and Venuvanalingam examined transition-state stabilization and destabilization in a different set of masked dienes.[12a]

Theoretical studies play an important role in understanding of the relative stabilities, reactivity and thermodynamic stability of series of reactant pairs.[8,9,13–15] Once a reliable computational method has been established, detailed calculations on a series of reactant pairs help in rationally designing feasible reaction pathways. Diels–Alder reactions of simple dienes and dienophiles have been studied extensively at various levels of theory,[13–15] but quantitative calculations on the masked dienes reaction profiles are limited. Previous computational studies have shown that the performance of the B3LYP method is much better than HF or MP2 methodologies in modeling Diels–Alder reactivity.[13,22–24]

We have reported detailed calculations on five-membered ring dienes with a standard dienophile and established that B3LYP/6–31G* is an optimal method for performing routine calculations on larger systems.[13a] We also have theoretically studied the Diels–Alder reactivities of [*c*]-annelated five-membered rings with both ethylene and acetylene as dienophiles.[8,9] The aim of the present study is to examine the reactivities of the cycloaddition reactions of cyclobutano[*b*]-, cyclobuteno[*b*]- and benzo[*b*]-fused five-membered ring dienes with ethylene and acetylene as dienophiles. The present study

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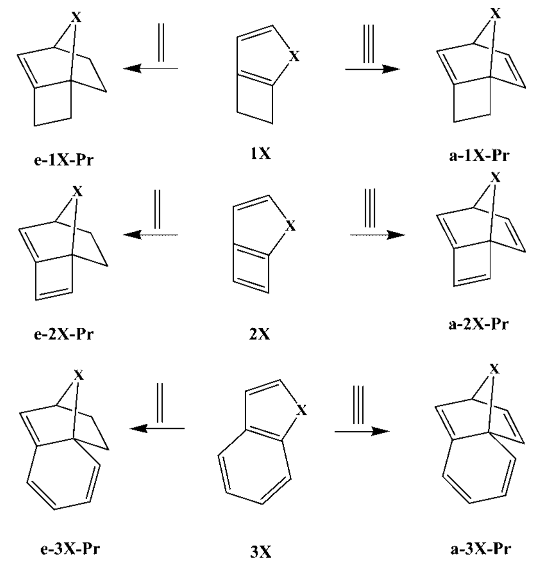


X = CH_2, SiH_2, NH, PH, O and S

Scheme 1

addresses how the Diels–Alder reactivity alters as a function of the position of annelation and the type of ring on the five-membered ring dienes by comparison with our recent studies reported for [*c*]-annelated dienes.[8,9] All the Diels–Alder reactions of [*c*]-annelated dienes considered in this study are depicted in Scheme 1. The activation and reaction energies with thermochemical data are used to predict the relative reactivities of the dienes considered with ethylene and acetylene as dienophiles. The distortion energies of the reactants at the transition states were calculated and analyzed.

COMPUTATIONAL METHODS

All the transition states and products of the cycloaddition reactions of each of the dienes with ethylene and acetylene were optimized at the B3LYP/6–31G* level. All the dienes and dienophiles were also optimized within the symmetry constraints. Frequency calculations were carried out to characterize all the reactants, transition states and products at the same level. The frequency calculations indicate that the planar forms of all the **PH** substituted dienes and all the dienes of **2X** type except **2SiH₂** are not minima on the potential energy surface. The imaginary frequencies obtained for these dienes were followed and the corresponding minimum energy structures were obtained. All the products have all real frequencies and the transition states possess one imaginary frequency. The bond orders were obtained using natural bond orbital (NBO)[25] method at the B3LYP/6–31G* level. All the calculations were performed using the Gaussian 98 suite of programs.[26] The values obtained in G3MP2 calculations on the model system **2CH₂** with acetylene are similar to those at the B3LYP level, which indicates that the chosen level of theory is adequate in terms of reliability. (The calculations carried out at the G3MP2 level for the reaction of **2CH₂** with acetylene give activation and reaction energies of 9.1 and $-63.5\,\mathrm{kcal\,mol^{-1}}$, respectively, which are in agreement with the B3LYP/6–31G* values of 10.4 and $-65.9\,\mathrm{kcal\,mol^{-1}}$ respectively. E.-U. Wuerthwein, personal communication.)

RESULTS AND DISCUSSION

We start with the description of equilibrium geometries followed by the relative preference for [*b*]- and [*c*]-annelation to a given five-membered ring. The activation and reaction energies along with the thermochemical correction are then given. This section culminates with the corroboration of the deformation energies with the activation barriers.

Equilibrium geometries

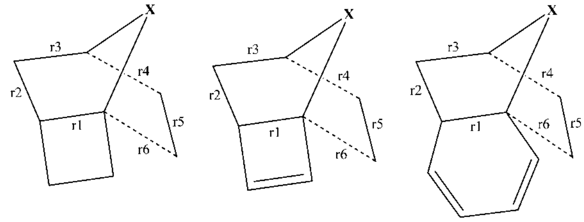
B3LYP/6–31G* optimizations were carried out on all the structures considered in the study and it was verified whether they are minima or true transition states by frequency calculations. The equilibrium geometries of the minima of all the dienes, the geometries of the transition states and products are given in the supplementary material. The principal bond lengths, which undergo significant changes along the reaction coordinate, in the transition states of the cycloaddition reactions considered are given in Tables 1 and 2; the designations and nomenclature used in this study are shown in Scheme 2.

Table 1. Principal bond lengths (Å) in the transition states of the cycloaddition reactions of dienes **1X**, **2X** and **3X** with ethylene (see Scheme 2 for designation and nomenclature)

	*r*1	*r*2	*r*3	*r*4	*r*5	*r*6
e-1CH₂-TS	1.389	1.402	1.405	2.294	1.386	2.226
e-1SiH₂-TS	1.407	1.402	1.407	2.256	1.396	2.242
e-*anti*-1NH-TS	1.414	1.372	1.440	2.198	1.403	2.118
e-*syn*-1PH-TS	1.397	1.393	1.407	2.271	1.394	2.226
e-*anti*-1PH-TS	1.410	1.391	1.414	2.266	1.391	2.227
e-1O-TS	1.397	1.379	1.430	2.217	1.394	2.154
e-1S-TS	1.412	1.373	1.430	2.201	1.400	2.188
e-2CH₂-TS	1.392	1.403	1.399	2.546	1.369	2.344
e-2SiH₂-TS	1.401	1.406	1.398	2.540	1.376	2.355
e-*anti*-2NH-TS	1.430	1.370	1.442	2.384	1.387	2.201
e-*syn*-2PH-TS	1.397	1.394	1.400	2.582	1.376	2.309
e-*anti*-2PH-TS	1.419	1.386	1.415	2.485	1.375	2.325
e-2O-TS	1.410	1.379	1.425	2.428	1.377	2.254
e-2S-TS	1.428	1.366	1.436	2.404	1.384	2.269
e-3CH₂-TS	1.446	1.402	1.420	1.955	1.411	2.275
e-3SiH₂-TS	1.455	1.408	1.421	1.963	1.420	2.273
e-*syn*-3NH-TS	1.452	1.393	1.431	1.934	1.415	2.229
e-*anti*-3NH-TS	1.462	1.380	1.445	1.894	1.430	2.154
e-*syn*-3PH-TS	1.448	1.400	1.420	1.933	1.418	2.316
e-*anti*-3PH-TS	1.453	1.400	1.423	1.965	1.412	2.278
e-3O-TS	1.451	1.384	1.435	1.916	1.420	2.178
e-3S-TS	1.457	1.387	1.431	1.934	1.420	2.245

Table 2. Principal bond lengths (Å) in the transition states of the cycloaddition reactions of dienes **1X**, **2X** and **3X** with acetylene (see Scheme 2 for designation and nomenclature)

	*r*1	*r*2	*r*3	*r*4	*r*5	*r*6
a-1CH$_2$-TS	1.386	1.405	1.401	2.325	1.238	2.230
a-1SiH$_2$-TS	1.397	1.410	1.396	2.314	1.240	2.264
a-*anti*-1NH-TS	1.413	1.374	1.436	2.273	1.250	2.103
a-*syn*-1PH-TS	1.391	1.398	1.399	2.309	1.241	2.233
a-*anti*-1PH-TS	1.407	1.393	1.409	2.304	1.241	2.223
a-1O-TS	1.396	1.378	1.428	2.258	1.244	2.148
a-1S-TS	1.412	1.373	1.429	2.230	1.247	2.181
a-2CH$_2$-TS	1.390	1.407	1.394	2.652	1.229	2.262
a-2SiH$_2$-TS	1.394	1.411	1.391	2.584	1.230	2.339
a-*anti*-2NH-TS	1.427	1.374	1.435	2.525	1.241	2.156
a-*syn*-2PH-TS	1.393	1.397	1.395	2.651	1.232	2.255
a-*anti*-2PH-TS	1.417	1.388	1.411	2.558	1.233	2.264
a-2O-TS	1.409	1.380	1.423	2.493	1.234	2.217
a-2S-TS	1.428	1.367	1.433	2.480	1.238	2.209
a-3CH$_2$-TS	1.440	1.408	1.418	1.919	1.253	2.402
a-3SiH$_2$-TS	1.446	1.417	1.409	1.977	1.253	2.372
a-*syn*-3NH-TS	1.449	1.396	1.434	1.887	1.257	2.335
a-*anti*-3NH-TS	1.457	1.383	1.447	1.844	1.267	2.291
a-*syn*-3PH-TS	1.441	1.407	1.412	1.931	1.254	2.418
a-*anti*-3PH-TS	1.447	1.405	1.422	1.917	1.253	2.414
a-3O-TS	1.448	1.388	1.436	1.881	1.259	2.277
a-3S-TS	1.454	1.390	1.433	1.880	1.259	2.364



e/a-1X-TS e/a-2X-TS e/a-3X-TS

Scheme 2

The equilibrium geometries indicate that the reactions of all the three classes of dienes considered follow the typical [4 + 2] cycloaddition with both ethylene and acetylene as dienophiles. It is interesting that whereas the benzo[*c*]-fused dienes were reported to follow an [8 + 2] cycloaddition route, benzo[*b*]-fused dienes follow [4 + 2] pathways.[8,9]

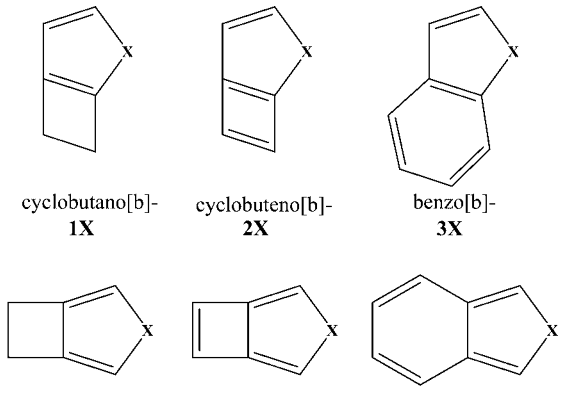
Tables 1 and 2 indicate that the deviation between the bond lengths of the forming σ-bonds are significantly larger (0.2–0.5 Å) in the case of the transition states of dienes **2X** and **3X**, indicating that the transition states are more unsymmetrical than the transition states of **1X**. **1-3NH** and their phosphorus analogues can yield both *syn* and *anti* products depending on the orientation of the pyramidal H attached to the heteroatom, and the *syn* and *anti* products were located and characterized as minima in all cases. The pyramidal hydrogen atom is oriented towards the diene side in the *syn* form whereas it is tilted towards the side of the incoming dienophile in the *anti* form. Both *syn* and *anti* transition states were obtained for the reaction of **3NH**, and all the attempts to locate the *syn* transition states were futile for **1NH** and **2NH** with both dienophiles. However, in the phosphorus analogues, **1-3PH**, no such problems were encountered and both *syn* and *anti* transition structures were obtained.

Relative energy differences between [*b*]- and [*c*]-annelated forms

Table 3 gives a comparison of the relative energies between [*b*]- and [*c*]-annelated five-membered rings (Scheme 3). The energies for the [*c*]-annelated dienes were taken from our previous studies.[8,9] The preference between [*b*]- and [*c*]-annelated positioning is marginal in the case of cyclobutane, a saturated ring. However, understandably, the saturated rings have a profound influence. Whereas the cyclobuteno ring has a high preference for [*c*]-annelation, benzoannelation has the exact opposite choice. The preference for [*c*]-annelation may be directly traced to the antiaromatic cyclobutadiene ring formation in the [*b*]-annelated diene. In contrast, when the fused ring is a benzenoid ring, it would prefer to retain the cyclic delocalization, which is possible only when it is annelated to the [*b*]-side of the five-membered ring. A closer look at the relative stabilities indicates that whereas the energy differences are high for annelation to

Table 3. Relative energies (kcal mol^{-1}) of [c]-annelated with respect to [*b*]-annelated forms for cyclobutano-, cyclobuteno- and benzo-fused cyclic five-membered ring dienes at the B3LYP/6–31G* level

	Cyclobutano-		Cylobuteno-		Benzo-	
Substituent	[*b*]	[*c*]	[*b*]	[*c*]	[*b*]	[*c*]
CH$_2$	0.0	−1.5	0.0	−31.9	0.0	22.6
SiH$_2$	0.0	−4.0	0.0	−39.0	0.0	24.3
NH	0.0	−1.6	0.0	−11.8	0.0	9.3
PH	0.0	−2.2	0.0	−28.4	0.0	18.7
O	0.0	−2.7	0.0	−19.3	0.0	14.5
S	0.0	−1.2	0.0	−19.0	0.0	11.2



cyclobutano[b]- **1X**
cyclobuteno[b]- **2X**
benzo[b]- **3X**
cyclobutano[c]-
cyclobuteno[c]-
benzo[c]-

Scheme 3

the non-aromatic (X = CH_2 and SiH_2) five-membered ring dienes, the gap is smaller for the aromatic ones (X = O, S, NH and PH).

Table 4. Activation energy ($\Delta E^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation for the cycloadditions of dienes **1X**, **2X** and **3X** with ethylene and acetylene obtained at the B3LYP/6–31G* level[a]

		$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}_{398\,K}$
$1CH_2$		18.6 (**19.7**)	19.5 (**20.2**)	−42.5 (**−38.8**)	36.4
$1SiH_2$		19.2 (**18.1**)	20.0 (**18.4**)	−42.9 (**−39.0**)	37.1
1NH	*anti*	25.9 (**26.2**)	26.7 (**26.6**)	− 43.7 (**−39.7**)	44.1
1PH	*syn*	23.8 (**24.1**)	24.5 (**24.3**)	−42.4 (**−38.4**)	41.3
	anti	23.3 (**24.5**)	24.1 (**24.8**)	−42.7 (**−38.7**)	41.1
1O		21.4 (**23.8**)	22.0 (**23.8**)	−42.6 (**−38.8**)	38.9
1S		31.9 (**34.3**)	32.5 (**34.3**)	−42.6 (**−38.7**)	49.4
$2CH_2$		8.3 (**10.0**)	9.2 (**10.4**)	−40.9 (**−35.9**)	25.5
$2SiH_2$		8.8 (**9.6**)	9.5 (**9.8**)	−44.0 (**−39.5**)	27.0
2NH	*anti*	15.4 (**16.2**)	16.1 (**16.4**)	−41.4 (**−36.8**)	32.6
2PH	*syn*	16.0 (**17.5**)	16.5 (**17.4**)	−39.7 (**−35.4**)	32.3
	anti	13.0 (**14.9**)	13.8 (**15.1**)	−41.0 (**−36.5**)	30.1
2O		10.7 (**13.4**)	11.4 (**13.5**)	−40.7 (**−36.4**)	27.6
2S		19.5 (**22.1**)	20.1 (**22.1**)	−41.5 (**−37.3**)	36.6
$3CH_2$		32.6 (**32.2**)	33.5 (**32.6**)	−42.6 (**−38.2**)	50.5
$3SiH_2$		33.4 (**30.6**)	34.0 (**30.7**)	−42.7 (**−38.7**)	51.0
3NH	*syn*	48.4 (**50.1**)	48.8 (**49.8**)	−42.7 (**−38.5**)	65.8
	anti	42.6 (**41.1**)	43.4 (**41.4**)	−43.2 (**−39.1**)	60.6
3PH	*syn*	35.2 (**34.1**)	35.9 (**34.3**)	−42.3 (**−38.1**)	52.8
	anti	37.2 (**37.2**)	37.9 (**37.4**)	−42.8 (**−38.4**)	54.9
3O		37.1 (**37.8**)	37.6 (**37.7**)	−42.1 (**−38.2**)	54.4
3S		44.2 (**45.5**)	44.8 (**45.5**)	−42.2 (**−38.0**)	61.6

[a] Gibbs free energies of activation at 398 K ($\Delta G^{\ddagger}_{398\,K}$) are given only for ethylene as dienophile. Entropies of activations are in eu and all other values are in kcal mol^{-1}. The values in parentheses in bold are for acetylene as dienophile.

Activation and reaction energies with thermochemical data

Activation energies, enthalpies and entropies of activation for the cycloaddition reactions of the [*b*]-annelated dienes considered with ethylene and acetylene are given in Table 4. Figure 1 illustrates the variation of the activation energies for the reactions of these three classes of dienes with both dienophiles. A cursory look at Fig. 1 shows that, in general, the activation energies required for the reactions involving acetylene as dienophile are slightly higher than those for ethylene reactions in all the three classes. This is in agreement with our previous computational studies on the cycloaddition reactions of simple and [*c*]-fused five-membered ring dienes with ethylene and acetylene as dienophiles.[9,13b,15] Figure 1 shows that the differences in activation energies between ethylene and acetylene reactions are higher for the cycloadditions of **O** and **S** substituted dienes in **1X** and **2X** types; these dienes with acetylene require about 2.5 kcal mol^{-1} (1 kcal = 4.184 kJ) higher activation energy than the reactions with ethylene as dienophile. Notably, the reaction of **$3SiH_2$** with acetylene requires about 3 kcal mol^{-1} lower activation energy than that of ethylene as dienophile. Table 4 shows that the activation energy ranges from 8 to 22 kcal mol^{-1} for the dienes **2X** and from 30 to 50 kcal mol^{-1} for the benzo[*b*]-fused dienes, **3X** with both dienophiles. The activation energy required for dienes **1X** lies in between those for **2X** and **3X** types, ranging from 18 to 35 kcal mol^{-1}. The lower activation energies observed for cyclobuteno[*b*]-fused dienes **2X** may be traced to the loss of unfavorable antiaromaticity due to the cyclobutadiene from reactant to transition state. The high activation energy required for the reactions of dienes **3X** among the three classes may be attributed to the loss of aromatic stabilization of the dienes while going from the reactant to the transition state. In contrast, our recent computational studies on [*c*]-fused systems indicated that benzo[*c*]-fused and cyclobuteno[*c*]-fused dienes require the lowest and highest activation energies, respectively.[8,9] The product stability accounted for the relative reactivities of [*c*]-annelated dienes; the aromatic benzenoid rings are formed in the products for the benzo[*c*]-fused dienes whereas the antiaromatic butadiene moieties resulted in the products for the cyclobuteno[*c*]-fused dienes. Hence the present study indicates that the loss of aromatic stabilization or the antiaromaticity induced by the annelated rings from the reactant to the transition state play an important role in determining the reactivities of the cycloaddition reactions.

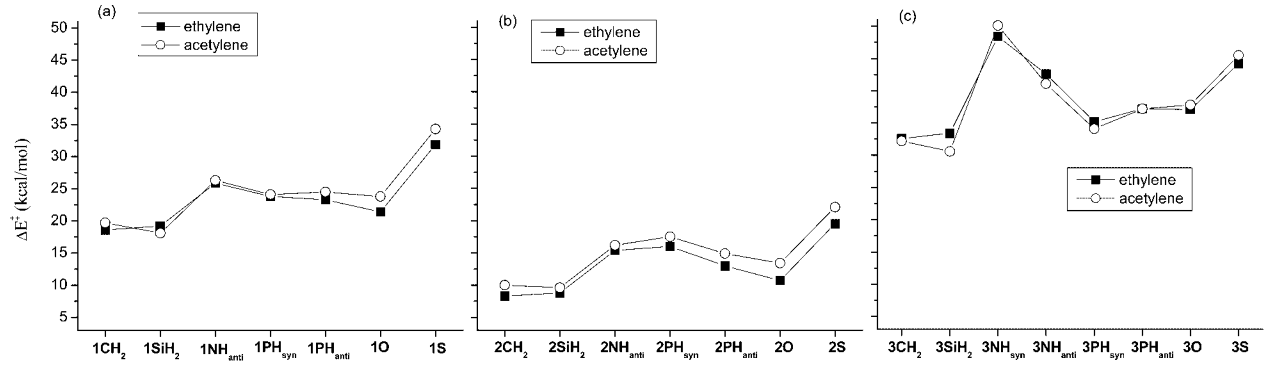


Figure 1. Variation in activation energies for the cycloaddition reactions of dienes (a) **1X**, (b) **2X** and (c) **3X** with ethylene and acetylene as dienophiles

Table 5. Reaction energies (ΔE_r), enthalpies (ΔH_r) and entropies (ΔS_r) of reactions for the cycloadditions of dienes **1X**, **2X** and **3X** with ethylene and acetylene obtained at the B3LYP/6–31G* level[a]

		ΔE_r	ΔH_r	ΔS_r	$\Delta G_{\mathrm{r398K}}$
1CH$_2$		−28.7 (**−37.3**)	−24.9 (**−33.7**)	−47.1 (**−44.5**)	−6.1
1SiH$_2$		−25.2 (**−42.5**)	−22.0 (**−39.3**)	−46.6 (**−44.4**)	−3.4
1NH	*syn*	−8.4 (**−12.8**)	−5.2 (**−10.0**)	−47.5 (**−44.6**)	13.7
	anti	−7.8 (**−14.3**)	−4.8 (**−11.4**)	−47.3 (**−44.7**)	14.1
1PH	*syn*	−21.4 (**−33.3**)	−17.9 (**−30.0**)	−46.7 (**−44.0**)	0.8
	anti	−24.1 (**−33.8**)	−20.6 (**−30.5**)	−46.6 (**−44.0**)	−2.0
1O		−18.4 (**−21.9**)	−15.5 (**−19.4**)	−46.4 (**−43.7**)	3.0
1S		−11.3 (**−15.5**)	−8.1 (**−12.7**)	−46.0 (**−43.0**)	10.2
2CH$_2$		−61.3 (**−70.4**)	−56.7 (**−65.9**)	−48.0 (**−45.4**)	−37.5
2SiH$_2$		−57.7 (**−74.4**)	−53.6 (**−70.4**)	−50.6 (**−48.3**)	−33.4
2NH	*syn*	−34.6 (**−40.1**)	−30.8 (**−36.6**)	−46.7 (**−44.0**)	−12.2
	anti	−33.3 (**−40.8**)	−29.7 (**−37.3**)	−46.7 (**−44.1**)	−11.0
2PH	*syn*	−52.1 (**−63.8**)	−47.8 (**−59.9**)	−47.1 (**−44.5**)	−29.0
	anti	−54.1 (**−63.8**)	−49.9 (**−59.8**)	−47.2 (**−44.6**)	−31.1
2O		−46.7 (**−51.6**)	−43.0 (**−48.2**)	−46.4 (**−43.8**)	−24.5
2S		−41.9 (**−47.0**)	−37.9 (**−43.4**)	−46.9 (**−44.1**)	−19.2
3CH$_2$		5.7 (**−2.5**)	8.9 (**0.5**)	−45.4 (**−42.8**)	27.0
3SiH$_2$		5.6 (**−11.6**)	8.3 (**−9.0**)	−45.0 (**−42.8**)	26.2
3NH	*syn*	22.0 (**18.0**)	25.0 (**20.6**)	−45.6 (**−42.8**)	43.2
	anti	25.1 (**19.1**)	27.8 (**21.6**)	−45.4 (**−42.7**)	45.9
3PH	*syn*	8.0 (**−4.0**)	11.1 (**−1.2**)	−45.2 (**−42.7**)	29.1
	anti	6.8 (**−3.0**)	9.8 (**−0.3**)	−45.2 (**−42.6**)	27.8
3O		15.8 (**12.7**)	18.4 (**14.9**)	−44.4 (**−41.7**)	36.1
3S		16.8 (**12.2**)	19.8 (**14.7**)	−44.6 (**−41.6**)	37.5

[a] Gibbs free energies of reactions at 398 K ($\Delta G_{\mathrm{r398\,K}}$) are given only for ethylene as dienophile. Entropies of reactions are in eu and all other values are in kcal mol^{-1}. The values in parentheses in bold are for acetylene as dienophile.

Table 4 shows that with both dienophiles, **CH$_2$** and **SiH$_2$** substituted dienes in all the three classes require lower activation energies than the heteroatom-substituted dienes, which possess a lone pair of electrons. This can be attributed to the participation of the lone pair of electrons of the heteroatoms in the delocalization in five-membered rings. In all three classes, **CH$_2$** and **SiH$_2$** substituted dienes are more reactive than all other dienes with ethylene and acetylene, respectively. The reactions of dienes **1S** and **2S** have the highest activation barriers correspondingly in **1X** and **2X** types with both dienophiles. For the reactions involving **NH** substituted dienes, both *syn* and *anti* transition states were obtained only for **3NH**. The formation of the *syn* transition state of **3NH** with both dienophiles requires the highest activation energy in **3X** type and this is followed by **3S**. The *syn* transition state of **3NH** lies about 6 kcal mol^{-1} higher in energy than the *anti* transition state for the ethylene reaction, whereas the *syn* transition state is about 9 kcal mol^{-1} above the *anti* form for acetylene as dienophile. The higher activation energy required for the formation of the *syn* transition state of **3NH** may be traced to the repulsive interactions between the nitrogen lone pair and the forming σ-bond in the transition state, similarly to the study of Domingo *et al.*[27] on the cycloaddition between *N*,*N′*-dipyrrolylmethane and hexafluorobut-2-yne. In the case of **PH** substituted dienes, except for the reaction of **1PH** with acetylene, the *anti* transition states lie below the *syn* transition states in **1PH** and **2PH**, whereas the reverse is observed in **3PH**. The activation energy difference between the *syn* and *anti* transition states in **1PH** is about 0.5 kcal mol^{-1}, but this difference is about 2.5–3.0 kcal mol^{-1} in the case of **2PH** and **3PH** with both dienophiles.

Table 5 lists the reaction energies, enthalpies and entropies of reactions for all the reactions considered. Figure 2 depicts the variation in reaction energies obtained for the reactions of all three classes of dienes with both the dienophiles. Tables 4 and 5 indicate that the reaction energies parallel the activation energies for these three classes. The reaction energy varies from −8 to −43 kcal mol^{-1} for **1X** type, from −33 to −75 kcal mol^{-1} for dienes **2X** and from 25 to −12 kcal mol^{-1} for **3X** type. Figure 2 illustrates that the trends obtained are very similar for all three classes. In contrast to the activation energies, the reaction exothermicities of the reactions involving acetylene are higher than those with ethylene as dienophile. This is in agreement with our previous computational studies.[9,13b,15] Figure 2 also shows that a significant difference in reaction energies is observed between ethylene and acetylene reactions for **SiH$_2$** and **PH** substituted dienes. The reactions of **SiH$_2$** substituted dienes with acetylene are about 17 kcal mol^{-1} more exothermic than the reactions with ethylene as dienophile. In general, the reactions of **CH$_2$** substituted dienes are the most exothermic in ethylene reactions whereas the reactions of **SiH$_2$** substituted dienes are predicted to be the most exothermic when acetylene is used as the dienophile. The reaction of **NH** substituted dienes with either ethylene or acetylene as dienophile is computed to

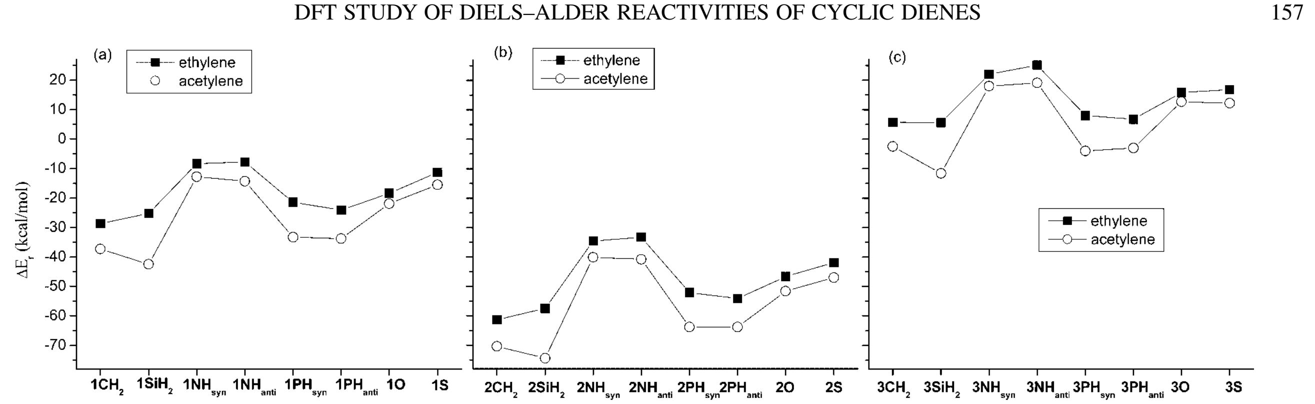


Figure 2. Variation in reaction energies for the cycloaddition reactions of dienes (a) **1X**, (b) **2X** and (c) **3X** with ethylene and acetylene as dienophiles

be the least exothermic consistently in all the three classes.

Except for the reactions of **$3CH_2$**, **$3SiH_2$** and **3PH** with acetylene, all other reactions considered for **3X** type are endothermic. The endothermicity of the reactions of dienes **3X** can be traced to the loss of aromatic stabilization of the reactant dienes. Hence the cycloaddition reactions of **3X** with dienophiles are not feasible under normal conditions. As the trends obtained are similar for the reactions of dienes with ethylene and acetylene as dienophiles, we computed the Gibbs free energies at 398 K only for ethylene reactions, and the values are given in Tables 4 and 5. The high Gibbs free energies of activation (about 50–66 kcal mol) and the positive reaction free energies with higher magnitudes virtually preclude cycloadditions of **3X** with the dienophiles considered. However, if the compounds **e/a-3X-Pr** are formed, they are very likely to undergo facile retro-Diels–Alder reactions. The very high exothermicities of the reactions of dienes **2X** may be attributed to the loss of antiaromaticity from reactants to products. This is in contrast to our previous computational studies on [*c*]-annelated five membered rings, where the reactions of benzo[*c*]-fused dienes are the most exothermic owing to the product stability from the formation of the aromatic benzenoid ring. In addition, the reactions of cyclobuteno[*c*]-annelated dienes are highly endothermic, since the products formed contain antiaromatic four-membered rings.[8,9] Hence the present study unequivocally indicates that the reactant stability plays a vital role in predicting the reactivities of [*b*]-annelated five-membered rings whereas the product stability determines the reactivity of [*c*]-fused dienes in cycloaddition reactions. Figure 3 shows a good linear correlation between the activation and reaction energies for the cycloaddition reactions of the dienes considered with both dienophiles.

Tables 4 and 5 show that the activation and reaction entropy values for the reactions of dienes with acetylene are less negative than for the reactions of the corresponding diene with ethylene as dienophile, indicating higher reactivity for the acetylene reactions than that of the reactions involving ethylene as dienophile. The entropies of activation are less negative for the dienes of **2X** type among the three classes in reactions with both the dienophiles, as shown in Table 4.

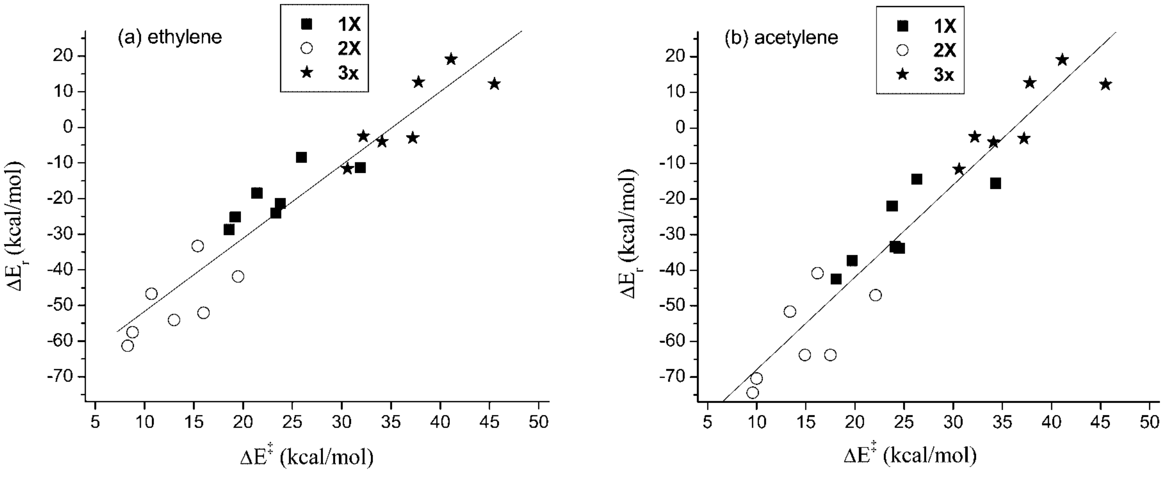


Figure 3. Plots showing the correlation between the activation energies and reaction energies for the reactions of the dienes considered with (a) ethylene and (b) acetylene

Bond order analysis

The estimation of bond orders gives the measure of the extent of bond making or bond breaking along the reaction pathway. By symmetry all the reactions considered cannot be synchronous; however, we assume that all the reactions follow the concerted pathway. Previous studies indicated that the concerted mechanism prevails over the stepwise alternative in most cases, even in the presence of adverse structural constraints.[28] We have computed the synchronicity (S_y) for the reactions considered using the previously reported equation:[29]

$$S_y = 1 - \frac{\sum_{i=1}^{n} \frac{|\delta B_i - \delta B_{\mathrm{av}}|}{\delta B_{\mathrm{av}}}}{2n-2} \qquad (1)$$

where n is the number of bonds directly involved in the reaction and δB_i is the relative variation of the bond order index B_i at the transition state:

$$\delta B_i = \frac{B_i^{\mathrm{TS}} - B_i^{\mathrm{R}}}{B_i^{\mathrm{P}} - B_i^{\mathrm{R}}} \qquad (2)$$

where the superscripts TS, R and P refer to the transition state, reactant and product, respectively. The average value of δB_i is denoted δB_{av} and is given by

$$\delta B_{\mathrm{av}} = \frac{1}{n}\sum_{i=1}^{n} \delta B_i \qquad (3)$$

The relative variation of bond order indices at the transition states for the bonds directly involved in the reactions and the synchronicity are given in Tables 6 and 7 for ethylene and acetylene reaction respectively. The numbering of the bond order indices corresponds to the bond length numberings shown in Scheme 2. Tables 6 and 7 show that the transition states formed for the reactions of dienes **2X** and **3X** are 'early' and 'late', respectively, among the three classes considered with both dienophiles. The reactions of dienes **2X** are more exothermic with 'early' transition state whereas the reactions of **3X** form 'late' transition states and almost all the reactions are endothermic. This is in agreement with Hammond's postulate.[30] The synchronicity values for the reactions of dienes **3X** are about 0.81–0.91, indicating that the reactions of **3X** are more asynchronous than those of **1X** and **2X** dienes. The synchronicity values are lower for the reactions of **3X** with acetylene than with ethylene. Hence the reactions of dienes **3X** with acetylene are more asynchronous than the reactions with ethylene as dienophile.

Deformation energies

The deformation energies of dienes and dienophiles, total deformation energies, interactions energies between diene and dienophile along with the activation energies for all the reactions considered are given in Table 8. The energy difference between the reactant in the transition state geometry and its corresponding equilibrium geometry gives the deformation energy. The interaction energy was calculated by subtracting the total deformation energy from the activation energy. Table 8 shows that the dienes and dienophiles are deformed to a lower extent in

Table 6. Variation of bond order indices (δB_1–δB_6) and synchronicities (S_y) obtained at the B3LYP/6–31G* level for the cycloaddition reactions of the dienes considered with ethylene

		δB_1	δB_2	δB_3	δB_4	δB_5	δB_6	δB_{av}	S_y
1CH$_2$		0.335	0.427	0.418	0.347	0.452	0.355	0.390	0.933
1SiH$_2$		0.382	0.463	0.464	0.389	0.510	0.385	0.432	0.935
1NH	*anti*	0.440	0.519	0.509	0.428	0.535	0.441	0.478	0.947
1PH	*syn*	0.344	0.415	0.413	0.380	0.498	0.383	0.406	0.946
	anti	0.382	0.469	0.463	0.374	0.473	0.374	0.423	0.935
1O		0.416	0.491	0.488	0.395	0.492	0.398	0.447	0.940
1S		0.422	0.490	0.497	0.422	0.517	0.408	0.459	0.945
2CH$_2$		0.298	0.359	0.324	0.231	0.342	0.281	0.306	0.930
2SiH$_2$		0.332	0.378	0.361	0.253	0.388	0.300	0.335	0.928
2NH	*anti*	0.442	0.480	0.452	0.328	0.448	0.381	0.422	0.936
2PH	*syn*	0.263	0.263	0.243	0.254	0.385	0.322	0.288	0.910
	anti	0.373	0.408	0.395	0.270	0.376	0.309	0.355	0.926
2O		0.397	0.432	0.408	0.284	0.392	0.330	0.374	0.929
2S		0.446	0.471	0.453	0.320	0.426	0.348	0.411	0.925
3CH$_2$		0.430	0.365	0.605	0.557	0.607	0.367	0.489	0.876
3SiH$_2$		0.468	0.384	0.620	0.569	0.642	0.393	0.513	0.886
3NH	*syn*	0.379	0.311	0.544	0.573	0.623	0.386	0.470	0.859
	anti	0.531	0.481	0.681	0.634	0.677	0.457	0.577	0.909
3PH	*syn*	0.438	0.365	0.612	0.584	0.637	0.367	0.500	0.867
	anti	0.446	0.387	0.614	0.553	0.604	0.372	0.496	0.886
3O		0.500	0.462	0.652	0.597	0.641	0.420	0.545	0.907
3S		0.472	0.438	0.630	0.584	0.633	0.398	0.526	0.897

Table 7. Variation of bond order indices (δB_1–δB_6) and synchronicities (S_y) obtained at the B3LYP/6–31G* level for the cycloaddition reactions of the dienes considered with acetylene

		δB_1	δB_2	δB_3	δB_4	δB_5	δB_6	δB_{ave}	S_y
1CH$_2$		0.296	0.381	0.365	0.293	0.375	0.310	0.337	0.934
1SiH$_2$		0.309	0.383	0.374	0.294	0.389	0.300	0.341	0.929
1NH	*anti*	0.389	0.466	0.434	0.356	0.453	0.406	0.417	0.952
1PH	*syn*	0.290	0.355	0.344	0.310	0.407	0.322	0.338	0.946
	anti	0.347	0.428	0.411	0.316	0.390	0.329	0.370	0.936
1O		0.384	0.452	0.441	0.344	0.425	0.366	0.402	0.936
1S		0.395	0.460	0.459	0.376	0.448	0.374	0.418	0.947
2CH$_2$		0.255	0.334	0.265	0.185	0.292	0.269	0.267	0.929
2SiH$_2$		0.279	0.323	0.298	0.192	0.300	0.247	0.273	0.921
2NH	*anti*	0.355	0.414	0.347	0.249	0.368	0.349	0.347	0.943
2PH	*syn*	0.221	0.246	0.205	0.197	0.323	0.282	0.246	0.908
	anti	0.333	0.379	0.339	0.223	0.316	0.288	0.313	0.926
2O		0.358	0.395	0.355	0.239	0.334	0.307	0.331	0.929
2S		0.407	0.446	0.399	0.272	0.368	0.332	0.371	0.925
3CH$_2$		0.367	0.276	0.574	0.533	0.531	0.531	0.272	0.830
3SiH$_2$		0.373	0.268	0.532	0.483	0.511	0.511	0.280	0.852
3NH	*syn*	0.328	0.240	0.536	0.569	0.573	0.573	0.309	0.812
	anti	0.467	0.381	0.661	0.630	0.619	0.619	0.352	0.863
3PH	*syn*	0.359	0.270	0.549	0.525	0.534	0.534	0.270	0.831
	anti	0.390	0.299	0.591	0.536	0.526	0.526	0.274	0.842
3O		0.447	0.388	0.629	0.585	0.586	0.586	0.340	0.874
3S		0.426	0.367	0.624	0.584	0.584	0.577	0.314	0.859

Table 8. Deformation energies of dienes and dienophiles, total deformation energies, interaction energies and activation energies ($\Delta E^{\ddagger}$) for the reactions of dienes **1X**, **2X** and **3X** with ethylene and acetylene as dienophiles[a]

		Deformation energy				
		Diene	Dienophile	Total	Interaction energy	$\Delta E^{\ddagger}$
1CH$_2$		15.5 (**14.5**)	7.1 (**9.6**)	22.6 (**24.1**)	−4.0 (−**4.4**)	18.6 (**19.7**)
1SiH$_2$		14.6 (**11.8**)	9.2 (**10.2**)	23.8 (**22.0**)	−4.6 (−**3.9**)	19.2 (**18.1**)
1NH	*anti*	21.4 (**20.3**)	11.8 (**15.2**)	33.2 (**35.5**)	−7.3 (−**9.3**)	25.9 (**26.2**)
1PH	*syn*	20.1 (**18.0**)	8.7 (**10.6**)	28.8 (**28.6**)	−5.5 (−**4.5**)	23.3 (**24.1**)
	anti	16.7 (**15.9**)	8.4 (**10.9**)	25.1 (**26.8**)	−1.3 (−**2.3**)	23.8 (**24.5**)
1O		18.4 (**18.1**)	9.1 (**12.4**)	27.5 (**30.5**)	−6.1 (−**6.7**)	21.4 (**23.8**)
1S		23.8 (**24.0**)	10.6 (**13.6**)	34.4 (**37.6**)	−2.5 (−**3.3**)	31.9 (**34.3**)
2CH$_2$		8.1 (**7.5**)	3.4 (**5.5**)	11.5 (**13.0**)	−3.2 (−**3.0**)	8.3 (**10.0**)
2SiH$_2$		8.3 (**7.3**)	4.2 (**5.6**)	12.5 (**12.9**)	−3.7 (−**3.3**)	8.8 (**9.6**)
2NH	*anti*	14.2 (**12.1**)	7.4 (**10.9**)	21.6 (**23.0**)	−6.2 (−**6.8**)	15.4 (**16.2**)
2PH	*syn*	15.7 (**14.8**)	4.3 (**6.0**)	20.0 (**20.8**)	−4.0 (−**3.3**)	16.0 (**17.5**)
	anti	10.3 (**9.8**)	4.5 (**6.9**)	14.8 (**16.7**)	−1.8 (−**1.8**)	13.0 (**14.9**)
2O		10.6 (**10.2**)	4.9 (**7.9**)	15.5 (**18.1**)	−4.8 (−**4.7**)	10.7 (**13.4**)
2S		15.7 (**15.5**)	6.3 (**9.3**)	22.0 (**24.8**)	−2.5 (−**2.7**)	19.5 (**22.1**)
3CH$_2$		22.9 (**20.6**)	13.3 (**15.4**)	36.2 (**36.0**)	−3.6 (−**3.8**)	32.6 (**32.2**)
3SiH$_2$		20.3 (**16.1**)	15.6 (**15.9**)	35.9 (**32.0**)	−2.5 (−**1.4**)	33.4 (**30.6**)
3NH	*syn*	37.9 (**37.0**)	14.0 (**16.9**)	51.9 (**53.9**)	−3.5 (−**3.8**)	48.4 (**50.1**)
	anti	31.9 (**29.7**)	18.9 (**22.5**)	50.8 (**52.2**)	−8.2 (−**11.1**)	42.6 (**41.1**)
3PH	*syn*	24.5 (**21.0**)	14.8 (**15.9**)	39.3 (**36.9**)	−4.1 (−**2.8**)	35.2 (**34.1**)
	anti	23.8 (**22.0**)	14.0 (**16.0**)	37.8 (**38.0**)	−0.6 (−**0.8**)	37.2 (**37.2**)
3O		28.1 (**26.7**)	15.6 (**18.6**)	43.7 (**45.3**)	−6.6 (−**7.5**)	37.1 (**37.8**)
3S		30.1 (**29.3**)	15.6 (**18.4**)	45.7 (**47.7**)	−1.5 (−**2.2**)	44.2 (**45.5**)

[a] All values are in kcal mol^{-1}. The values in parentheses in bold are for acetylene as dienophile.

the transition states obtained for **2X** dienes whereas the dienes **3X** and the dienophiles are deformed to a greater extent in the transition states of **3X**. The deformation energy data are indicative of lower and higher activation energies obtained for the reactions of dienes **2X** and **3X**, respectively. The deformation energy for acetylene is higher than for ethylene, which may be traced to the stronger π-bond strength of the former than the latter. The deformation energies of dienophiles explain the discrepancy in activation and reaction energies between ethylene and acetylene reactions. $\mathbf{CH_2}$ and $\mathbf{SiH_2}$ substituted dienes have lower deformation energies than other dienes in all the three classes. The total deformation energies obtained for **NH** and **S** substituted dienes are comparable, and the interaction energy values are more negative for the **NH** substituted dienes in all three classes irrespective of the dienophile considered. In general, the diene that requires a high activation energy deformed to a larger extent and vice versa.

CONCLUSIONS

We have reported B3LYP/6–31G* calculations on the cycloaddition reactions of cyclobutano[*b*]-, cyclobuteno[*b*]- and benzo[*b*]-fused five-membered ring dienes with ethylene and acetylene as dienophiles. The computed activation and reaction energies were compared with the previously reported results on the cycloaddition reactions of [*c*]-annelated five-membered rings with the dienophiles considered.[8,9] The activation and reaction energies reveal that the reactant stability seems to determine the reactivity of [*b*]-fused five-membered ring dienes. However, the product stability determines the barrier heights of the cycloaddition reactions in the [*c*]-annelated dienes. The **3X** type of dienes were found to be less reactive since the aromatic stability of the diene is lost on going to the transition state and then to the product. The present study concludes that Diels–Alder reactions of **3X** are difficult under normal conditions owing to positive free energies of reactions, whereas the retro-Diels–Alder reactions will be more feasible. The computations indicate that the reactions of dienes **2X** type require lower activation energies and are highly exothermic with both dienophiles because the antiaromicity induced by cyclobuteno annelation is lost in the product.

A comparison between the two dienophiles considered reveals that the activation energies for the acetylene reactions are slightly higher than those for the ethylene reactions, which is similar also in the [*c*]-annelated cyclic five-membered dienes.[8,9] The relative stability of [*b*]- and [*c*]-annelated reactants also depends on the extension of the aromatic stabilization or lack of it upon annelation. The reactions of dienes with acetylene are more exothermic than those with ethylene as dienophile. The deformation energies are lower and higher for **2X** and **3X** type of dienes, respectively, which is in consistent with the activation energies. All three classes of dienes follow $[4+2]$ cycloaddition reactions with both dienophiles. The transition states obtained for most of the reactions of dienes of **2X** and **3X** types are more asynchronous than those obtained for **1X**. A good linear correlation between activation and reaction energies is obtained for the reactions considered. The present study suggests that once the reactants of **2X** are available, the Diels–Alder reactions with dienophiles will readily proceed to give the products. However, the retro-Diels–Alder reactions of the products of **3X** are predicted to be more viable compared with the Diels-Alder reactions. Hence experimental attempts in this direction may be worthwhile.

Supplementary material

Figures and Tables giving the principal geometric parameters of all the dienes, transition states and products obtained at the B3LYP/6–31G* level and their optimized Cartesian coordinates and FMO energies are available at the epoc website at http://www.wiley.com/epoc.

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