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# The trimerization of acetylenes involves a cascade of biradical and pericyclic processes†

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Thorough computational studies were performed on mechanisms and energies for the thermal trimerizations of neutral or electron-rich acetylenes used as cross-linkers in organic hard-masks for lithography applications. These studies indicate that the operative mechanism proceeds through initial cyclobutadiene formation *via* a biradical mechanism. Cyclobutadienes form Dewar benzenes *via* Diels–Alder cycloadditions, or biradical processes, or both, before producing benzenes by electrocyclic ring-opening reactions. These pathways are preferred to alternatives involving concerted trimerizations or mechanisms involving carbene intermediates.

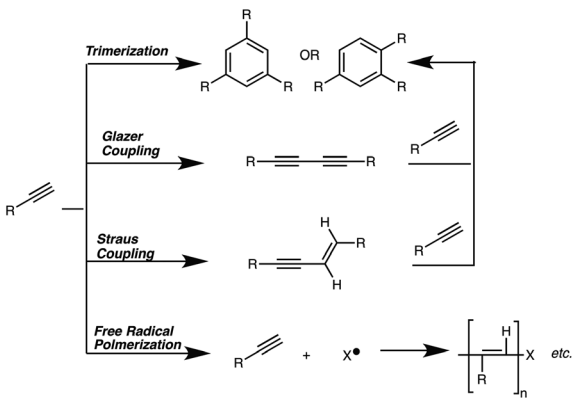


## Introduction

The use of cross-linkable functional groups to manufacture organic hard masks for lithography represents an important feature for semiconductor applications.[1] Organic hard-mask films are commonly decorated with alkynyl substituents[2–6] that possess the propensity to cross-link thereby limiting outgassing of oligomeric materials that may contaminate the manufacturing process.[1] Given that trace impurities could compromise device performance, metal catalysts are undesirable for these types of device applications; consequently such acetylene-containing molecules are typically thermally cured between ~200 and ~350 °C to promote cross-linking. Despite their widespread use, the nature of the products formed by cross-linking these alkynyl substituents is subject to much debate.

Scheme 1 shows proposed structural motifs for compounds that could arise from the cross-linking of alkynes. One of the more common proposals involves the formation of substituted benzenes.[4] Other proposals for cross-linked products involves the formation of directly linked diynes *via* Glaser-type coupling,[7] or enynes *via* the Straus reaction.[8] It has been noted that, once formed, these Glaser- or Straus-type products may be converted into substituted benzenes by reactions with an additional molecule of the acetylene.[4] Finally, free radical polymerization mechanisms have also been proposed.[4,9]

Herein we will focus primarily on mechanisms for the cross-linking of alkynyl groups to form substituted benzenes.




**Scheme 1** Proposed structures derived from acetylene cross-linking.

These studies involve the use of phenylacetylene and methylacetylene as models for ethynyl and propargyl arenes commonly used as cross-linking groups to manufacture organic hard masks.

Various mechanisms have been proposed for the formation of substituted benzenes derived from acetylene cross-linking. Scheme 2 shows some of the more common proposals. The thermal [2 + 2 + 2] reaction of acetylenes[4] which is commonly known to be promoted by transition metal catalysts[10,11] is one such. Alternative mechanisms will be investigated in which cyclobutadienes are formed by biradical processes[12,13] or processes in which carbene intermediates are formed. Biradical processes have been proposed for reactions involving electron-deficient acetylenes,[13] it has yet to be established whether such mechanisms are also operative for acetylenes substituted with electron-neutral or electron-rich groups such as alkyl or aryl substituents. It has been noted that phenylacetylene is not prone to dimerize, but that phenyl-1,3-butadiyne and higher

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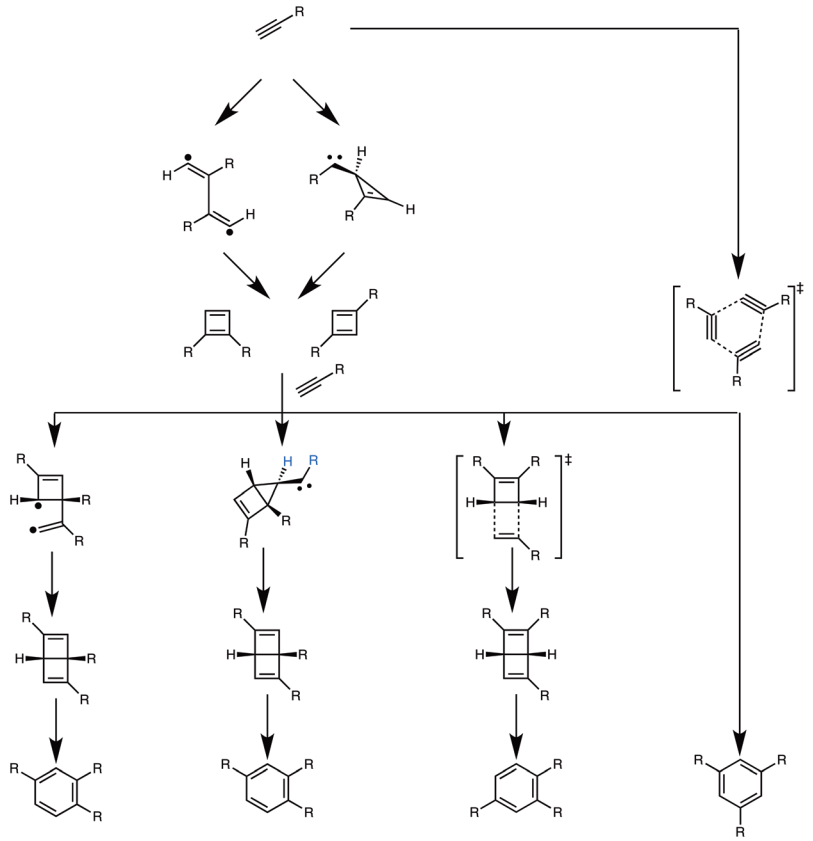

**Scheme 2** Various mechanisms for benzene formation from acetylene cross-linking.

oligoalkynes are susceptible to dimerization and formation of 1,3-butadiene-1,4-diyl biradicals.[14] Notably, the Bergman cyclization and related cyclizations features the formation of biradicals[15] in mechanisms that are evocative of acetylene dimerization *via* the biradical pathways studied herein.

Once formed, cyclobutadienes could then react with a third acetylene molecule *via* a biradical, carbene or Diels–Alder pathway to form Dewar benzenes which may then rearrange into benzene products. The latter process is noteworthy, since the thermal electrocyclic ring opening of the cyclobutene ring present in Dewar benzene occurs *via* a conrotatory motion, in contrast to a disrotatory process, which results in the formation of benzene with a *trans* double bond.[16–21]

## Computational methods

Calculations were performed using the GAMESS-US[22–24] suite of computational programs with the dispersion-corrected[25] UB3LYP[26–29] method (UB3LYP-D3). Structures were optimized and frequencies were computed using the 6-31G(d) basis set. It has been previously noted that (U)B3LYP/6-31G(d) is in qualitative agreement with calculations using (U)B3LYP/6-311++G(d,p)//6-31G(d).[13] Normal modes of all structures were examined to verify that equilibrium structures possess no imaginary frequencies and that one imaginary frequency corresponding to bond formation or bond breaking was obtained for transition state structures. Note that some processes involve low-barrier bond rotations that possess very low imaginary frequencies. Potential energy scans were performed for such processes and the highest energy constrained structures obtained from such scans were subjected to hessian calculations to obtain estimated free energies of transition structures. Intrinsic reaction coordinate (IRC) calculations were also performed to verify that transition states are connected to reactant complexes and intermediates on the free energy surfaces of reactions. Gas-phase free energies in kcal $mol^{-1}$ have been reported throughout the manuscript. Calculations were performed on the singlet free energy surface. Triplet contamination of singlet species were accounted for with YJH spin-projections[30] where necessary.

## Results and discussion

The predicted free energies of activation for the thermally allowed[17,19,31] [2 + 2 + 2] cycloaddition of phenylacetylene and methylacetylene to form 1,3,5-trisubstituted benzene are 76 and 73 kcal $mol^{-1}$, respectively (Fig. 1).

The bimolecular addition of two molecules of phenylacetylene or methylacetylene to form cyclobutadienes may occur *via* two different stepwise processes, shown in Fig. 2 and 3,

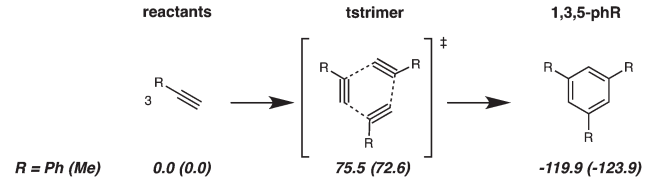


Fig. 1 Structures and free energies, in kcal mol$^{-1}$, for the [2 + 2 + 2] trimerization of phenylacetylene and methylacetylene (in parentheses).

both of which are predicted to possess comparatively smaller barriers than the [2 + 2+2] mechanism.

One of these mechanisms involves initial formation of substituted cyclopropenyl carbene intermediates, INT1c, that lie 50 and 49 kcal mol$^{-1}$ above the energies of phenylacetylene and methylacetylene reactants, respectively. TS1c, the transition state from which INT1c is formed, possesses free energies of 53 and 60 kcal mol$^{-1}$, respectively. This carbene can ring-close by forming a bond between the carbene moiety and either end of the cyclic alkene addend. The free energy barriers for ring-closure to form 1,2-disubstituted cyclobutadienes (int2_12) and 1,3-disubstituted cyclobutadienes (int2_13) are similar, 56 and 57 kcal mol$^{-1}$ for the reactions involving phenylacetylene and 51 and 52 kcal mol$^{-1}$, for the reactions involving methylacteylene. The dimethylcyclobutadienes possess similar free energies: they are about 1 kcal mol$^{-1}$ less stable than the reactants, but 1,2-diphenylcyclobutadiene is about 5 kcal mol$^{-1}$ more stable than the phenylacetylene reactants, while 1,3-diphenylcyclobutadiene is 11 kcal mol$^{-1}$ less stable than the reactants. The latter case is presumably due to the fact that 1,3-diphenylcyclobutadiene

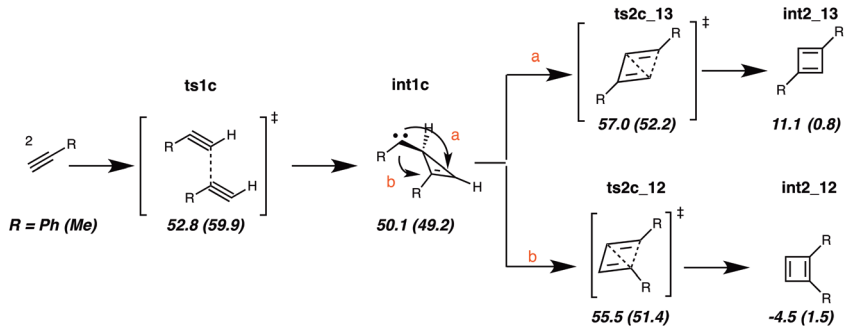


Fig. 2 Structures and free energies, in kcal mol$^{-1}$, for the dimerization of phenylacetylene and methylacetylene (in parentheses) *via* carbene formation.

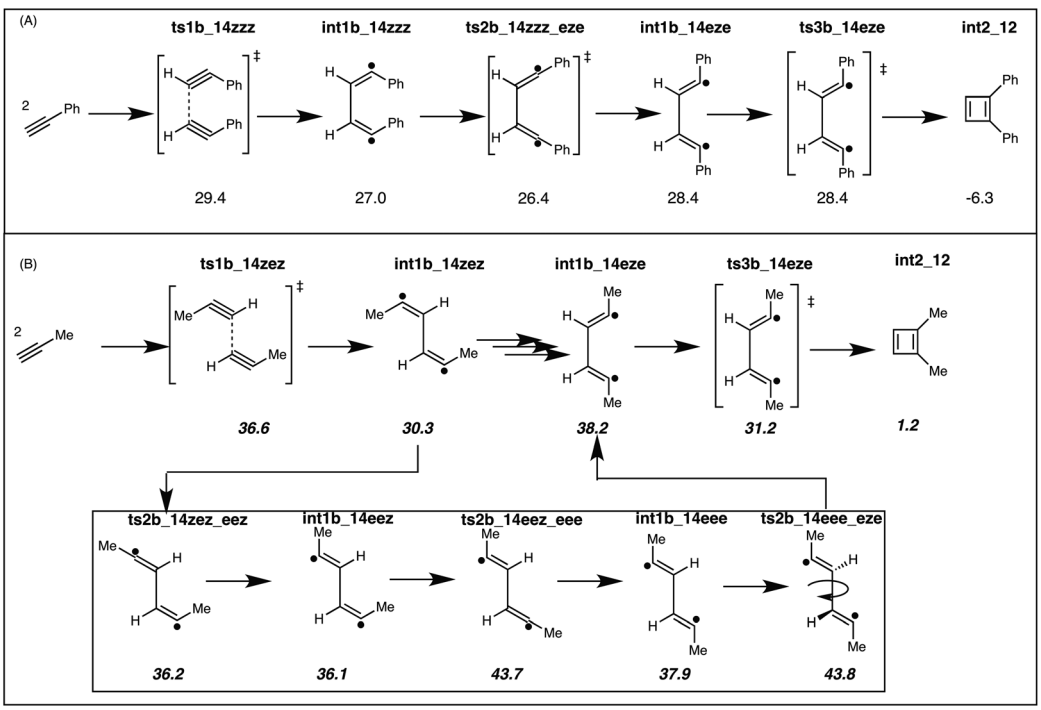


Fig. 3 Structures and free energies, in kcal mol$^{-1}$, for the dimerization of (a) phenylacetylene and (b) methylacetylene *via* biradical pathways.

 

adopts an anti-aromatic structure with all C–C bond lengths in the cyclobutadiene ring being a similar distance.

The alternative mechanism involves initial formation of biradical intermediates. The reactions involving phenylacetylene and methylacetylene (Fig. 3) occur *via* slightly different pathways. The free energy barrier for the addition of two phenylacetylenes in ts1b_14zzz is 29 kcal mol$^{-1}$ (Fig. 3a). This process forms int1b_14zzz which must be converted into int1b_14eze which possesses the geometry required for formation of int2_12. The free energy surface for the process is rather flat, the energies of the intermediates and transition structures lying along this path (including int1b_14zzz ts2b_14zzz_eze, ts2b_14zzz_eze, int1b_14eze and ts3b_14eze) are all approximately 27–28 kcal mol$^{-1}$.

Notably, a transition structure for the dimerization of phenylacetylene with a geometry similar to ts1b_14zzz could not be found for methylacetylene. Instead, ts1b_14zez, the initial transition structure for the dimerization of methylacetylene (Fig. 3b), could be located. It is predicted to possess a free energy barrier of 37 kcal mol$^{-1}$ and leads to the biradical intermediate int1b_14zez. For the cyclobutadiene intermediate to be formed from this biradical intermediate, a series of *cis–trans* rotations around the double bonds must occur to convert int1b_14zez into int1b_14eze, the biradical leading to the formation of int2_12 (Fig. 3, inset). These series of biradicals possess free energies ranging from 30–38 kcal mol$^{-1}$, and the barriers for *cis–trans* rotations range from 36–44 kcal mol$^{-1}$. The largest free energy barrier, 44 kcal mol$^{-1}$, involves conversion of int1b_14eez into int1b_14eee. The free energy barrier for C–C bond formation in ts3b_14eze is 31 kcal mol$^{-1}$.

Overall, formation of 1,2-disubstituted cyclobutadienes proceeds *via* a biradical pathway which is more favourable than the carbene process by about 8 kcal mol$^{-1}$. Note that 1,3-disubstituted cyclobutadienes are not formed *via* the biradical process, since this pathway would necessarily involve formation of biradical precursors in which one of the radical centres is not stabilized by a phenyl or methyl substituent.

Once the 1,2-disubstituted cyclobutadiene is formed, the production of trisubstituted benzenes proceeds by initial addition of a third molecule of methylacetylene leading to Dewar benzene intermediates *via* a biradical mechanism or *via* Diels–Alder cycloaddition shown in Fig. 4 and 5, respectively.

The biradical mechanism involves initial formation of vinylcyclobutene biradicals by the addition of either of the H- or Ph-terminated carbons of phenylacetylene (H- or Me-terminated carbons in the case of methylacetylene) to one of the double bonds in the cyclobutadiene. The mechanism of the reaction involving addition of the H-terminated carbon of phenylacetylene and methylacetylene to cyclobutadiene and associated stationary points are shown in Fig. 3. The lowest energy transition structure, ts5bhh_12, involves the addition of the H-terminated carbon of phenylacetylene or methylacetylene to C3 on int2_12. The free energies of activation for this addition are about 22 kcal mol$^{-1}$ for reactions involving methylacetylene and phenylacetylene; these are 1 and 2 kcal mol$^{-1}$ lower than the barrier to form the other biradical intermediate corresponding to addition to one of the Ph- or Me-substituted carbons on cyclobutadiene. The biradical formed after this addition, int3bhh_12, lies 16 kcal mol$^{-1}$ above the phenylacetylene substrates (3 kcal mol$^{-1}$ for the reaction involving methylacetylene).

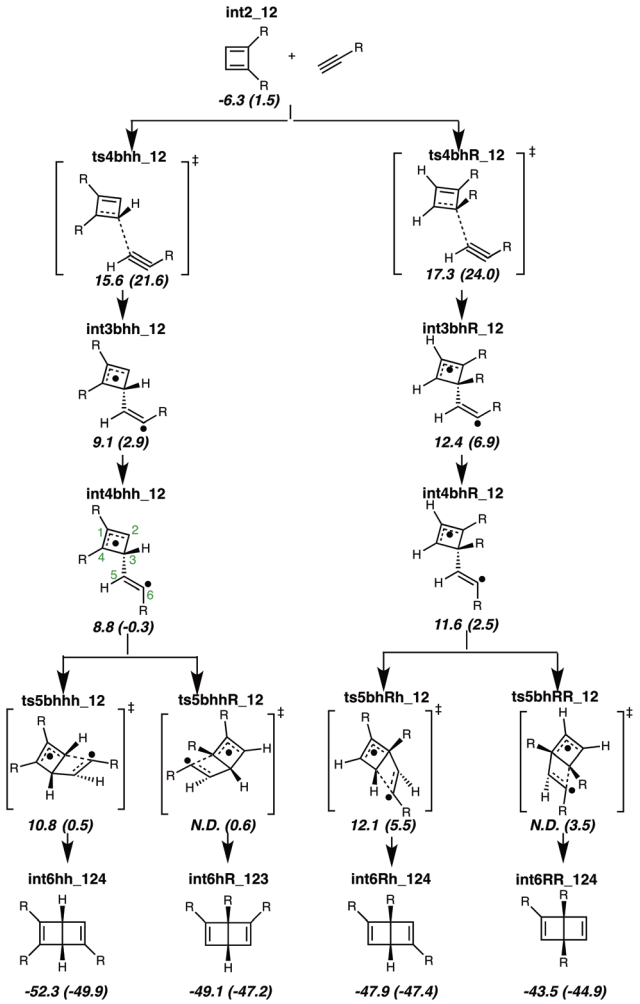


**Fig. 4** Structures and free energies, in kcal mol$^{-1}$, for Dewar benzene formation from reactions of substituted cyclobutadienes with phenylacetylene and methylacetylene (in parentheses). [n.d. = not determined].

Notably, the free energies of activation corresponding to addition of the Ph- or Me-terminated carbon of phenylacetylene or methylacetylene to the substituted cyclobutadienes (not shown) are 4–14 kcal mol$^{-1}$ larger than the barriers for addition of the H-terminated carbon of the substituted acetylenes to the cyclobutadiene.

These biradicals then undergo a low energy conversion of the *Z* conformation of the substituents the vinyl radical moiety into *E* isomers with free energy barriers less than 2 kcal mol$^{-1}$ (see ESI† for details). These series of int4 isomers can then directly convert into Dewar benzenes by rotation around the C3–C5 bond. These processes possess low rotation barriers of less than 2 kcal mol$^{-1}$ with respect to the int4 series.

Note that carbene intermediates may be directly formed from the series of int3 biradicals, but is less favourable than

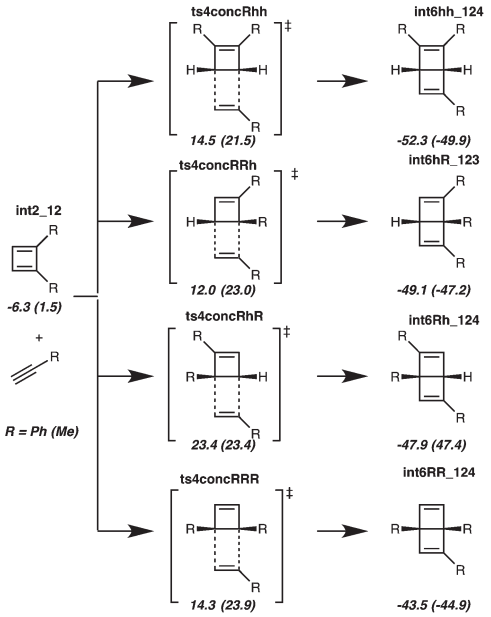


Fig. 5 Structures and free energies, in kcal mol$^{-1}$, for the Diels–Alder reactions of cyclobutadienes with phenylacetylene and methylacetylene (in parentheses).

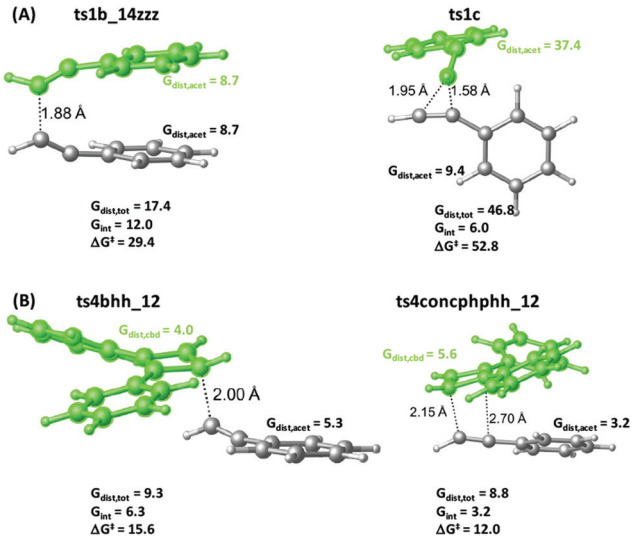


Fig. 6 Transition structures and free energies, in kcal mol$^{-1}$, for the (a) dimerization of phenylacetylene by biradical and carbene mechanisms (b) addition of phenylacetylene to 1,2-diphenylcyclobutadiene by biradical and Diels–Alder mechanisms. Distortion energies of the acetylene ($G_{dist,acet}$), cyclobutadiene ($G_{dist,cbd}$) and the sum $G_{(dist,tot)}$ are shown, as well as interaction energies ($G_{tot}$).

the direct conversion of the biradicals into Dewar benzenes (see ESI† for details).

Overall, these calculations suggest that Dewar benzenes may be formed from vinylcyclobutene biradicals that readily cyclize *via* low-barrier rotations.

Alternative Diels–Alder reactions leading to Dewar benzene formation involve the concerted but nearly synchronous addition of methylacetylene to int2_12 (Fig. 5). The most favourable transition structure for the reaction of phenylacetylene with 1,2-diphenylcyclobutadiene is ts4concphphh which possesses a free energy of activation of 18 kcal mol$^{-1}$ with respect to the low-lying cyclobutadiene, and is favoured over other transition structures by at least 2 kcal mol$^{-1}$. Similarly, the most favourable Diels–Alder transition structure for the reaction involving methylacetylene, ts4concmehh_12 lies 22 kcal mol$^{-1}$ above the reactants and is predicted to be more favourable than other Diels–Alder transition structures by at least 2 kcal mol$^{-1}$.

Importantly, Diels–Alder reactions to form Dewar benzenes from reactions involving phenylacetylene are predicted to be at least 4 kcal mol$^{-1}$ more favourable than biradical pathways. Conversely the most favoured pathways for reactions involving methylacetylene proceed *via* Diels–Alder reactions or biradical pathways. This result is in contrast to previous results involving reactions of electron-deficient alkynes, for which biradical formation from cyclobutadiene was predicted to be more favourable than Diels–Alder cycloaddition.[13]

The preference for various mechanisms predicted for cyclobutadiene formation and Dewar benzene formation can be explained by the distortion/interaction–activation strain model.[32–39] In this model, the free energies of activation of these reactions are derived from the combination of the energies required to distort the reactants into the transition state geometries, and the energies derived from the interactions of the distorted fragments.

Fig. 6 and 7 show that the distortion free energies for all transition structures are typically low (ranging from 1 to

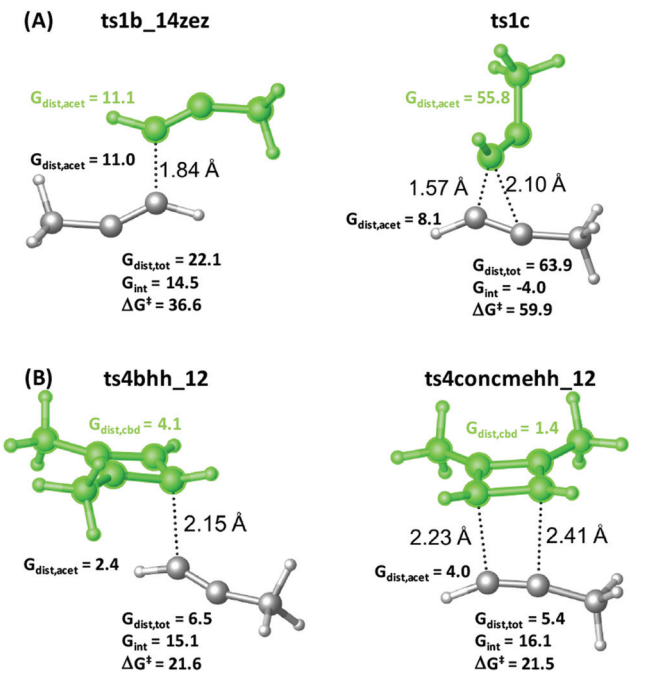


Fig. 7 Transition structures and free energies, in kcal mol$^{-1}$, for the (a) dimerization of methylacetylene by biradical and carbene mechanisms (b) addition of methylacetylene to 1,2-dimethylcyclobutadiene by biradical and Diels–Alder mechanisms. Distortion energies of the acetylene ($G_{dist,acet}$), cyclobutadiene ($G_{dist,cbd}$) and the sum $G_{(dist,tot)}$ are shown, as well as interaction energies ($G_{tot}$).

 

11 kcal mol$^{-1}$) with the exception of processes involving carbene formation. For these transition structures, one of the reacting phenylacetylene and methylacetylene fragments is strained to such a degree that the distortion free energies are 37 and 56 kcal mol$^{-1}$, respectively. By contrast, the interaction free energies of these transition structures are typically destabilizing and are approximately 3 to 12 kcal mol$^{-1}$ for reactions involving phenylacetylene and approximately 15 kcal mol$^{-1}$ for reactions involving methylacetylene; the lone exception is ts1c for the reaction involving methylacetylene which is stabilized by 4 kcal mol$^{-1}$.

Overall for cyclobutadiene formation, the sizeable energies required to distort the interacting fragments into geometries required to form carbenes are reinforced or mitigated to only a slight degree by the interactions of the distorted fragments. As a result, the free energy barriers for carbene formation are much larger than those for analogous barriers for biradical formation, for which distortion energies are much smaller.

The preference for Diels–Alder cycloaddition over the biradical mechanism during Dewar benzene formation for the reaction involving phenylacetylene is primarily due to the interaction energies of the reacting fragments. The total free energy required to distort the cyclobutadiene and phenylacetylene fragments are approximately the same for the biradical and Diels–Alder TSs, about 9 kcal mol$^{-1}$. However, due to better orbital overlap between 1,2-diphenylcyclobutadiene and phenylacetylene in the Diels–Alder TS in contrast to the bi-

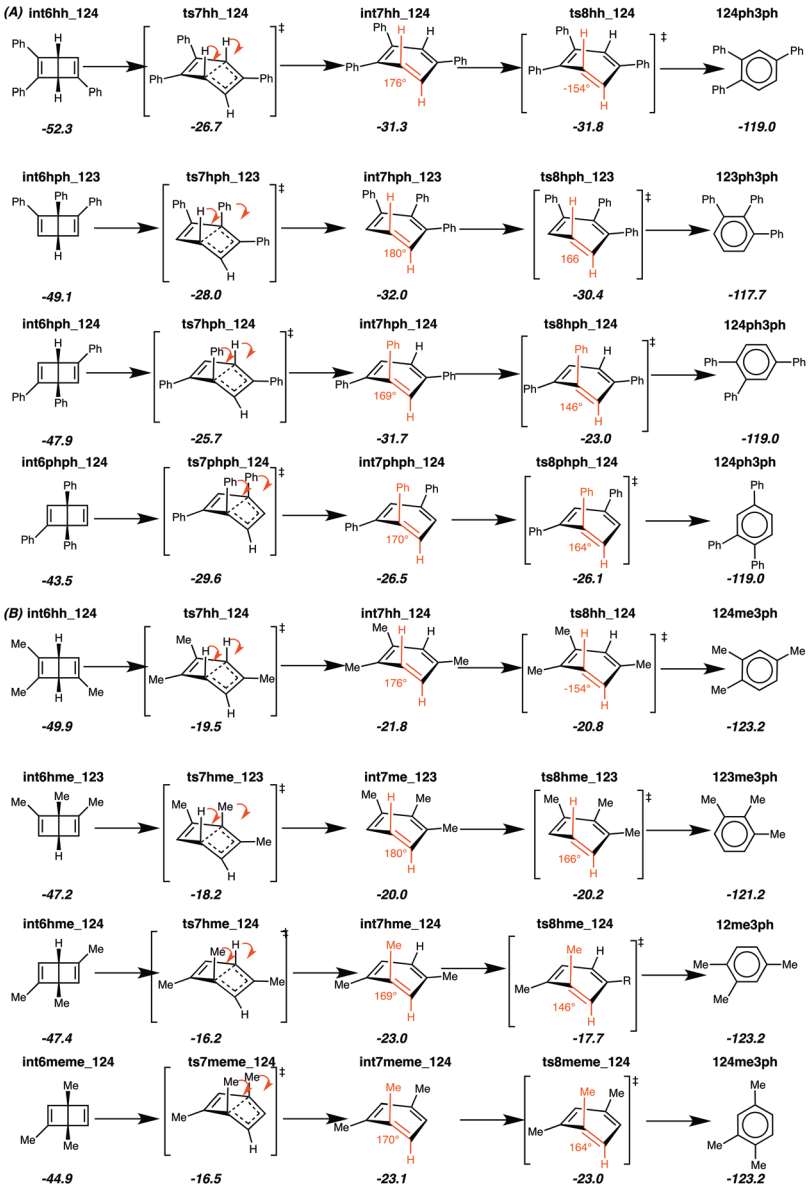


**Fig. 8** Structures and free energies, in kcal mol$^{-1}$, for benzene formation from (a) phenyl- and (b) methyl-substituted Dewar benzenes.

radical TS, the interaction energy is less destabilizing and thus the free energy barrier is lower.

In the case of Dewar benzene formation from methylacetylene, the total distortion energies and the interaction energies for the biradical and the Diels–Alder processes are approximately equal, and therefore the free energy barriers for both types of mechanisms are almost equal.

The predicted mechanism for the thermal conversion of Dewar benzene to benzene involves initial formation of *trans*-benzene by conrotatory ring-opening (Fig. 8). The free barriers for the ring-opening of all the Dewar benzene isomers (int6) proceeding from int2_12 are very similar, ranging from only 28 to 31 kcal $mol^{-1}$ in the case of methylacetylene, and 14 to 26 kcal $mol^{-1}$ in the case of phenylacetylene. The lowest energy barrier for the ring-opening of both the phenyl- and methyl-derived Dewar benzenes involves int6phph_124 and int6meme_124, respectively. This is presumably due to the fact that these intermediates are relatively less stable than other related intermediates (by 4 to 9 kcal $mol^{-1}$ for the triphenylated Dewar benzenes and by 2 to 5 kcal $mol^{-1}$ for reactions involving trimethylated Dewar benzenes), likely due to steric interactions between neighbouring phenyl and methyl groups on the Dewar benzene bridge. *trans*-Benzenes lie in shallow wells, 21 to 28 kcal $mol^{-1}$ above the energy of the Dewar benzenes from which they are formed; their conversion into the benzene products is a low barrier process with transition structures lying 1–6 kcal $mol^{-1}$ above the *trans*-benzene intermediates (17 to 29 kcal $mol^{-1}$ with respect to the low-lying Dewar benzenes).

Finally, it is instructive to note that the rate-determining step for both reactions involves initial acetylene dimerization, for which the reaction involving phenylacetylene possesses a lower free energy of activation than that involving the dimerization of methylacetylene.

## Conclusions

In summary, various mechanisms have been investigated for benzene formation by the thermal trimerization of methylacetylene and phenylacetylene, models for the cross-linking of propargyl and ethynyl arenes. Calculations indicate that benzene formation initially involve the dimerization of two acetylene molecules *via* a biradical mechanism which is favoured over carbene formation. Cyclobutadienes formed from the dimerization process then react with another acetylene molecule to form Dewar benzenes *via* Diels–Alder cycloaddition, in the case of the reaction involving phenylacetylene, or *via* equally favourable Diels–Alder cycloaddition or vinylcyclobutene biradical formation in the case of reactions involving methylacetylene. These preferences were explained by the use of the distortion/interaction-activation strain model. The transformation of Dewar benzenes into benzene under the thermal conditions of these reactions involve initial formation of *trans*-benzene intermediates *via* electrocyclic ring-opening. These lie in shallow wells and are readily converted into benzenes by *cis–trans* rotation.

## Conflicts of interest

There are no conflicts to declare.

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