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Butterflyene: an entry into an aesthetically pleasing carbocycle *via* a Diels–Alder reaction on a tetrasubstituted olefin†

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An interesting molecular architecture, butterflyene, resembling the shape of a butterfly has been synthesized *via* a sequence of cyclocondensation, benzylic oxidation, McMurry coupling and Diels–Alder reaction (DAR), successively. The DAR of the tetrasubstituted double bond of a bicyclopentylidene moiety with various dienes has been performed to prepare the analogues of butterflyene. DFT calculations have also been used to analyze the structural optimization and reaction energies.

Introduction

The synthesis of interesting molecular architectures with strained and sterically hindered molecular features is a formidable task for synthetic chemists.[1] Such molecules have aesthetic beauty, unusual synthesis challenges, and unique characteristics such as chirality, supramolecular assembly, and optical and electronic properties, which make them promising candidates for OFET and OLED applications.[2] Moreover, such molecules are valuable as synthons in the synthesis of many natural products and non-natural products.[3] To enhance such applications, often polycyclic aromatic hydrocarbons (PAHs) with a complex carboskeleton with fascinating geometries have been explored.[4,5] Trindane is one such promising scaffold which has been found in various symmetric carbocyclic frameworks as shown in Fig. 1.[6–9]

Our synthetic studies towards such scaffolds[10,11] prompted us to explore new carbocycles possessing fascinating molecular architectures. In the present communication, we demonstrate a synthetic protocol towards acquisition of an interesting molecular geometry resembling the shape of a butterfly in four simple steps from cyclopentanone without using complex and fancy reagents. Based on our continued research interest in designing architecturally pleasing molecules,[12–14] we contemplated that the shape of an open-winged butterfly (Fig. 2a) could be envisioned as that in Fig. 2b in which one of the peripheral cyclopentane rings of two trindane units (held together by a small ring) overlapping with each other would appear just as shown in the figure. Upon further simplification, the carbocyclic skeleton in Fig. 2b would furnish the structure shown in Fig. 2c. In view of our recent engagement in trindane chemistry,[10] we reckoned the wings of the butterfly as trindane moieties connected by a small bicyclic system as antennae located on the head of the butterfly. Similarly, the close-winged butterfly in Fig. 2d was envisioned as a molecule having the framework shown in Fig. 2e, in which both the trindane units completely overlap with each other, giving a skeleton as shown in Fig. 2f.

As shown in Fig. 3, this prototype decacyclic ring system was thought to be assembled *via* a Diels–Alder cycloaddition reaction of **7** and a suitable diene. For this purpose, cyclopentadiene was chosen because of its easy accessibility and better reactivity in cycloaddition reactions.

Bitrindanylidine **7** was easily recognized as a McMurry dimer of the trindanone unit **6**, which has been synthesized from cyclopentanone in two easy steps. The shape of the minimized energy structure calculated for butterflyene **8** using DFT coincides with the shape of a butterfly and hence we coined the term butterflyene for it.

Results and discussion

At the outset, our synthetic efforts commenced with the preparation of trindane **5** by acid-catalyzed cyclocondensation of cyclopentanone in dry ethanol[15] to deliver **5** as a white solid in 32% yield (Scheme 1). The thus-obtained trindane was sub-

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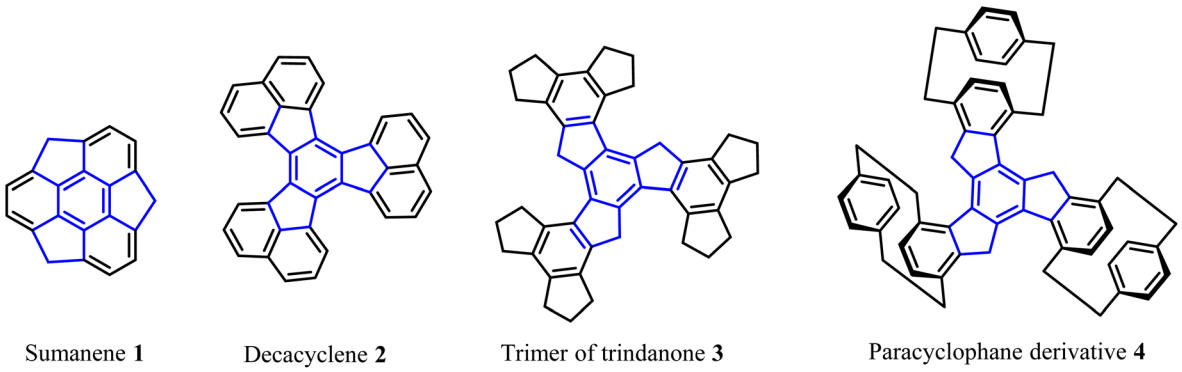


Fig. 1 Aesthetic symmetric architectures having a trindane scaffold.

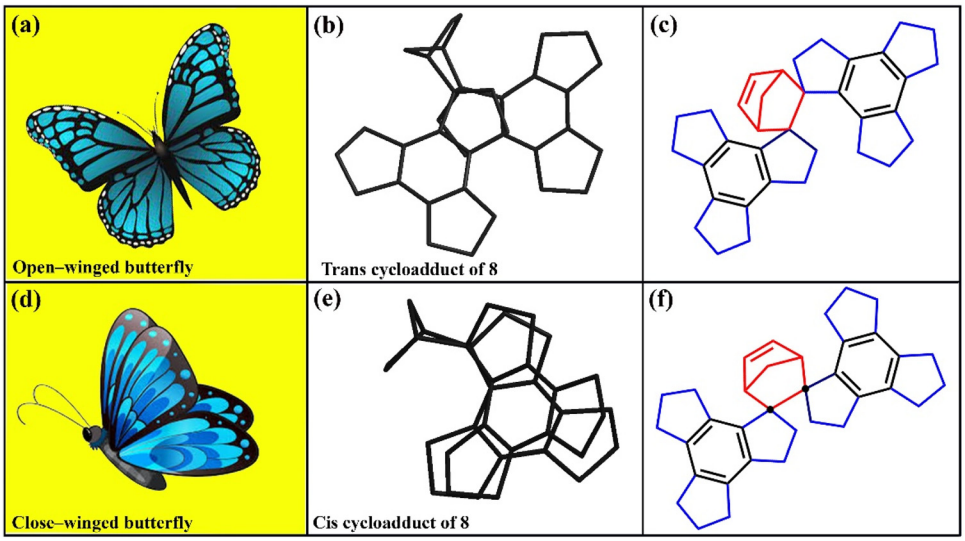


Fig. 2 DFT model visualization of the *cis* and *trans* cycloadducts of butterflyene.

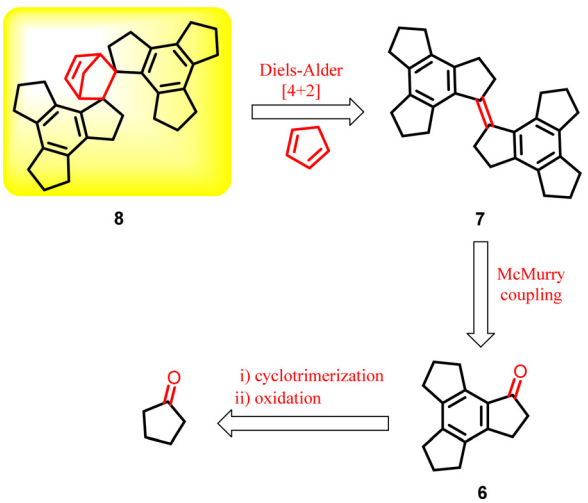
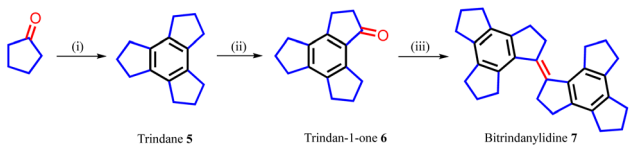


Fig. 3 Retrosynthetic plan for butterflyene **8**.



Scheme 1 Preparation of the McMurry product **7**. (i) Conc. H_2SO_4, dry EtOH, reflux, 15 h; (ii) $Na_2Cr_2O_7$, AcOH, 80 °C, 0.5 h; (iii) $TiCl_4$, Zn, dry THF, 0 °C, 12 h.

jected to oxidation using sodium dichromate to furnish its benzylic monoketone **6** (TLC).[8] Ketone **6** was purified by column chromatography and obtained as a white solid in 56% yield.

The McMurry reaction[16] is a classic example of deoxygenative coupling of carbonyl compounds leading to the formation of alkenes, where low-valent titanium species have been found

to promote the reaction of aldehydes/ketones to furnish alkenes *via* dimerization of ketyl radicals by one-electron reduction of the carbonyl groups. Accordingly, we attempted the synthesis of a symmetric olefinic system **7** by reductive dimerization of **6** using the McMurry homocoupling reaction. For this, low-valent titanium was initially prepared by the reduction of $TiCl_4$ using activated zinc dust in dry THF at 0 °C under an argon blanket. Into the above mixture was introduced the solution of ketone **6** in THF slowly in a dropwise manner. The reaction mixture was stirred at ambient temperature for 12 h and was monitored by TLC. The subsequent workup and chromatography of the reaction mixture furnished bitrindanylidine **7** as a white solid (mp 218 °C) in 40% yield (Scheme 1). The structure of compound **7** was fully discernible from its spectral data. Thus, bitrindanylidine **7** exhibited bands at 1433 cm^{-1}, indicating the aromatic C=C stretching in its IR spectrum. The proton NMR spectrum (600 MHz, $CDCl_3$) showed multiplets at δ 2.92–2.72 (m, 24H), confirming the presence of benzylic and allylic protons along with the homobenzylic protons showing signals between δ 2.20 and 2.02 (m, 8H). The ^{13}C NMR (151 MHz, $CDCl_3$) of **7** displayed six signals at δ 140.24, 139.44, 139.19, 138.26, 137.76 and 137.22 for two aromatic rings along with one signal at δ 135.78 for the olefinic exocyclic C=C bond. In addition, eight signals at δ 37.45, 34.69, 31.66, 31.40, 31.01, 30.56, 27.06 and 25.56 for a total of sixteen carbons on cyclopentane rings were also observed.

While proceeding towards the synthesis of the target molecule butterflyene **8**, we envisaged the difficulties associated with the Diels–Alder reaction (DAR) on a tetrasubstituted olefin. When we looked into the literature, we found only a handful of examples of the DAR on tetrasubstituted double bonds in an *intra*- and *inter*-molecular fashion.[17,18] There were no examples of the DAR of bicycloalkylidenes, except that of bicyclopropylidene **11**, which was a similar one to our system **7**.[19] Moreover, the double bond in bicyclopropylidene **11** was reported to be reactive due to the strain involved in the cyclopropane rings. The reason for cycloaddition between **13** and $\mathbf{D_1}$ to form cycloadduct **14** was attributed to EWGs in the dienophile **13**.[20]

Based on the above information, we anticipated a sluggish DAR of **7** as it is a relatively bulky molecule. This may have a substantial bearing on the rate and outcome of its cycloaddition with the diene. It should be noted that the tetrasubstituted double bond in bitrindanylidine **7** has neither any type of strain like that present in a cyclopropane ring in **11** nor is it activated by any electron-withdrawing group like that in **13** (Fig. 4a and b).

The DAR between **7** and freshly cracked cyclopentadiene $\mathbf{D_1}$ (with intermittent portionwise addition) in toluene under reflux met with no success as envisioned. Taking clue from this observation, we then attempted the DAR of **7** with neat dicyclopentadiene in a sealed tube at 180 °C for 24 h to furnish the cycloadduct **8** in 85% yield (Scheme 2).

Proton NMR spectra of butterflyene **8** indicated it to be a *cis* and *trans* mixture. It showed signals at δ 5.99, 5.61 and 5.44,

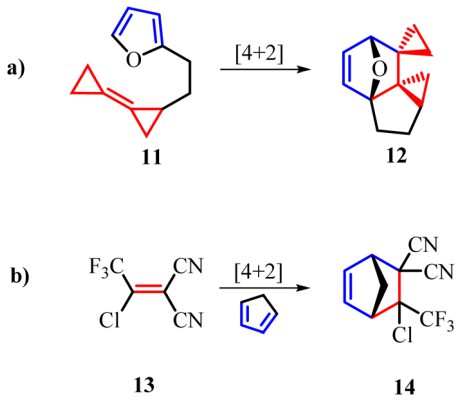
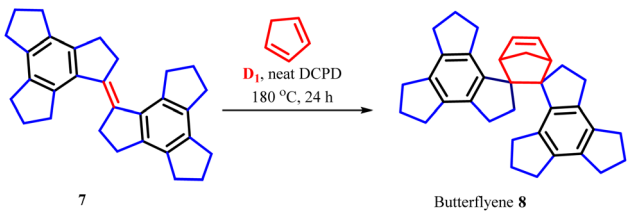


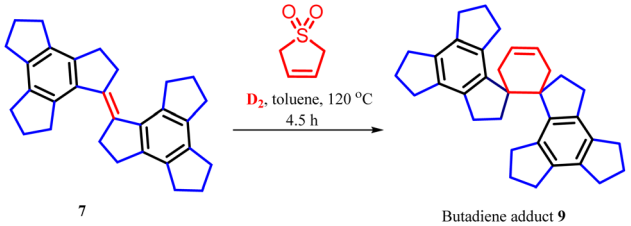
Fig. 4 (a) Intramolecular DAR of the strain-activated double bond in bicyclopropylidene **11**.[19] (b) DAR of tetrasubstituted ethylene activated by EWGs in **13**.[20]



Scheme 2 Synthesis of butterflyene **8**.

indicating the presence of olefinic protons in the cycloadducts (as mixture), resulting from the *cis*- and *trans*- isomers of **8** in the proportion of 79 : 21. Unfortunately, we could not separate the crystals of pure isomers of **8** from one another.

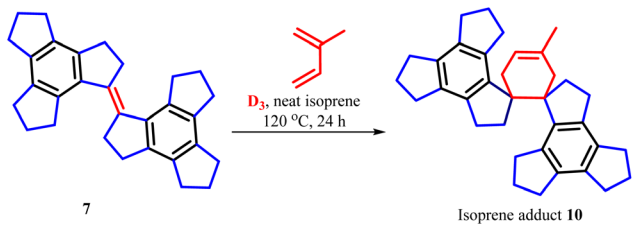
To the best of our knowledge, this is the first report of a tetrasubstituted double bond of a bicyclopentylidene moiety undergoing a DAR with diene. It is noteworthy to observe that $\mathbf{D_1}$ despite being a reactive diene underwent cycloaddition with the tetrasubstituted olefin under relatively difficult conditions. Prompted by this result, we examined the cycloaddition of the hindered dienophile **7** with some more dienes ($\mathbf{D_2}$–$\mathbf{D_6}$). Fortuitously, we also succeeded in preparing the analogues of **8** such as butadiene adduct **9** and isoprene adduct **10**. Initially, butadiene ($\mathbf{D_2}$) gas was generated *in situ* using butadiene sulfone in toluene at 80 °C and bitrindanylidine **7** was added slowly while increasing the temperature to 120 °C. The reaction was complete after 4.5 h to furnish the butadiene adduct **9** as a white solid in 80% yield (Scheme 3).



Scheme 3 Synthesis of the butadiene adduct **10** of compound **7**.

The structure of the compound **9** was deduced from its spectral features. Its proton NMR (500 MHz, $CDCl_3$) showed signals at δ 5.54 and 4.52 for olefinic protons on the cyclohexene ring in a ratio of 66 : 34, indicating it to be a mixture of *cis* and *trans* isomers as expected. ^{13}C NMR (151 MHz, $CDCl_3$) displayed signals at δ 147.36–134.10, revealing the presence of carbons of the central benzene rings along with the signal at δ 127.11, confirming the presence of olefinic carbons of the cyclohexene ring in **9**.

The isoprene adduct **10** was also prepared similarly from the McMurry product **7** and isoprene ($\mathbf{D_3}$) to furnish a white solid after column chromatography in 86% yield (Scheme 4). The proton NMR spectrum (600 MHz) of **10** showed signals at δ 5.52 and δ 4.49 for olefinic protons, indicating it to be a *cis*/*trans* mixture in a ratio of 66 : 34, respectively. Moreover, ^{13}C NMR (151 MHz, $CDCl_3$) of **10** displayed resonances at δ 140.23–127.18 for fourteen aromatic and olefinic carbons.



Scheme 4 Synthesis of the isoprene adduct **10** of compound **7**.

Interestingly, a substantial difference in shielding of the olefinic protons in the adducts **9** and **10** was observed in proton nuclear resonances compared to that in **8**. This is presumably because of the rigidly locked conformation due to the methylene bridge in adduct **8**, which is absent in **9** and **10**. In line with magnetic anisotropies in the case of **9** and **10**, it is reasonable to surmise that one of the olefinic protons may experience magnetic deshielding arising from the central benzene rings of trindane moieties, owing to the absence of the methylene bridge.

As can be envisaged from Fig. 5, the double bond in the *trans* isomer of **7** is more hindered than that in the *cis* isomer. Furthermore, it is interesting to observe that the addition with cyclic diene $\mathbf{D_1}$ in the DAR seems to be more difficult than that with acyclic dienes $\mathbf{D_2}$ and $\mathbf{D_3}$ due to the presence of the methylene group in $\mathbf{D_1}$, which perhaps makes the diene bulkier. The consequences of the above observations imply the formation of the *cis* and *trans* product mixture. The cyclic diene $\mathbf{D_1}$ furnished the corresponding *cis* cycloadduct **8** in 79% yield, while the corresponding *trans* adduct **8** in 21% yield. On the other hand, the acyclic dienes $\mathbf{D_2}$ and $\mathbf{D_3}$ were found to be able to reach the hindered double bond in the *trans* isomer **7** to a better extent and thus furnished the corresponding *trans* cycloadducts in a higher proportion than that in the case of $\mathbf{D_1}$ (34%). The acyclic dienes $\mathbf{D_2}$ and $\mathbf{D_3}$ furnished the corresponding *cis* cycloadducts as major products in 66% yield. The pictorial DAR is presented in Fig. 6. It is clearly evident that the DAR with all the dienes ($\mathbf{D_1}$–$\mathbf{D_3}$) is favored

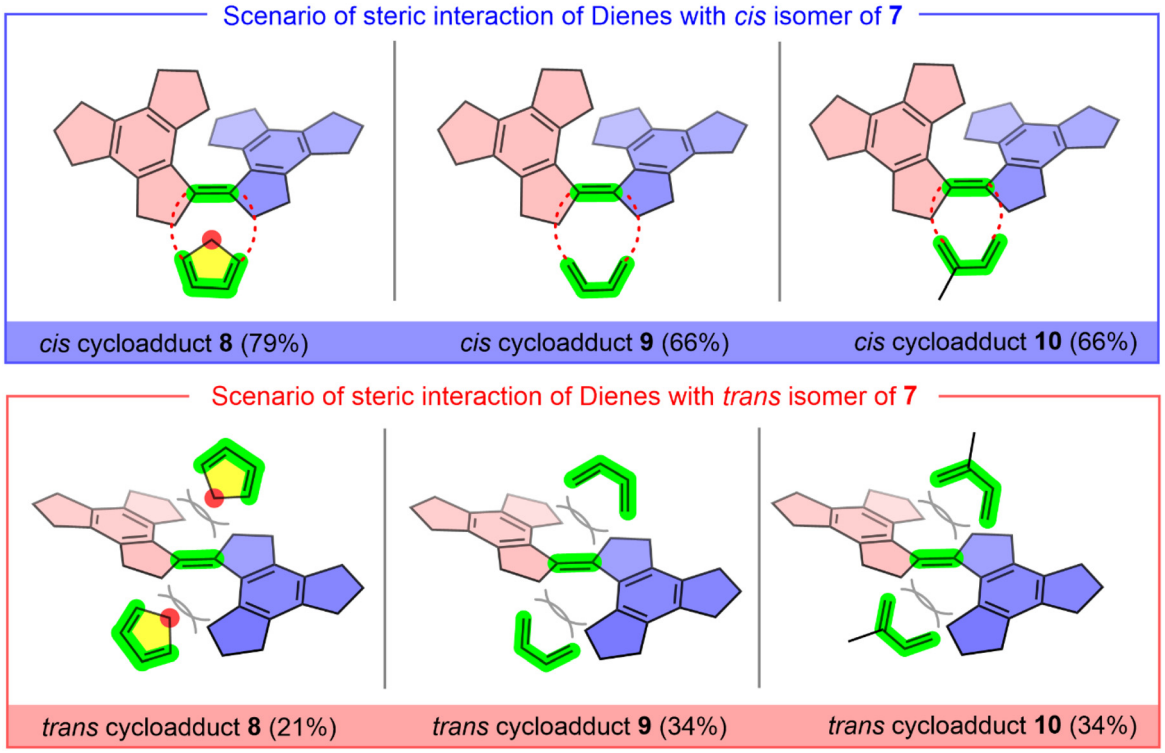


Fig. 5 Interaction between the *cis*/*trans* isomers of **7** with incoming dienes (figures in parenthesis indicate the percentage of relative olefinic peak intensities).

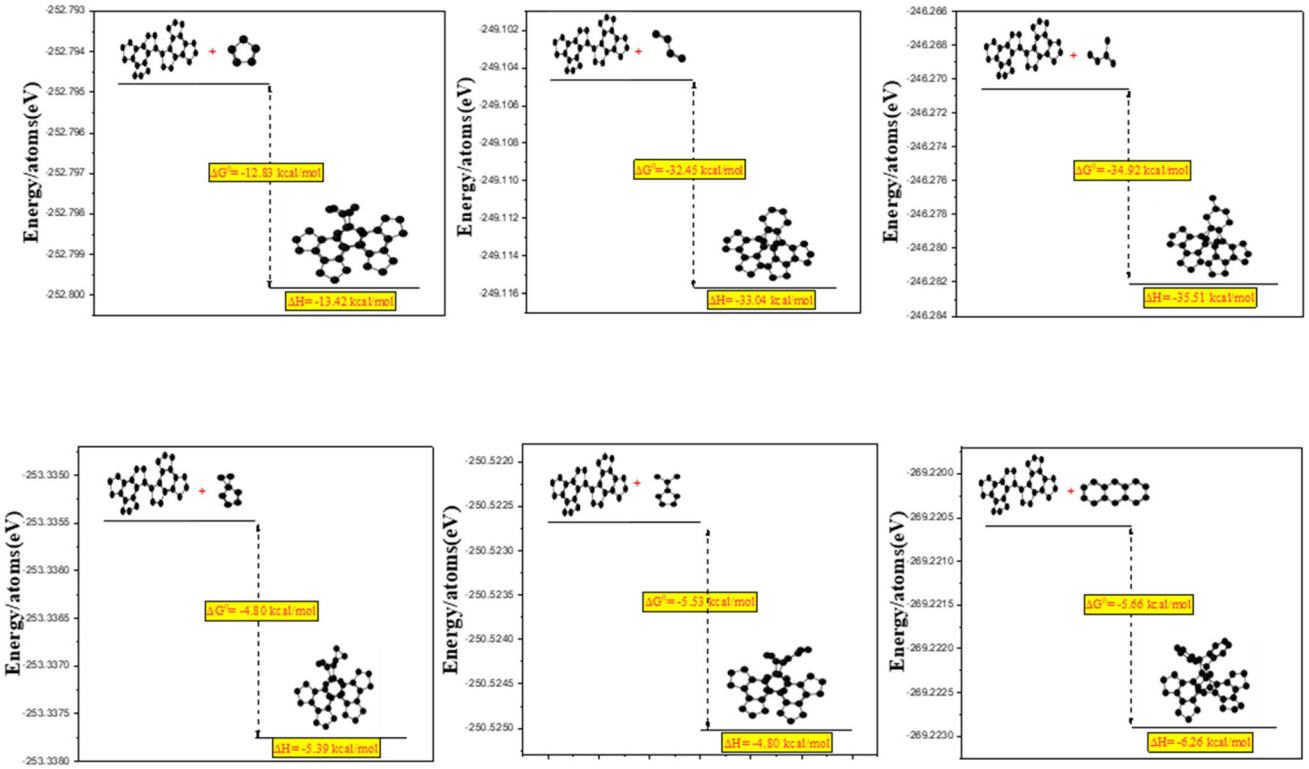


Fig. 6 Reaction coordinate diagram of the cycloadducts of various dienes D_1–D_6.

from the less hindered face from the opposite side of two trindane units in 7 to afford the corresponding cycloadducts.

Next, we evaluated the scope of the DAR between 7 and dienes, *viz.* 6,6-dimethylfulvene (**D_4**), spiro[2.4]hepta-4,6-diene (**D_5**) and anthracene (**D_6**). We encountered difficulties upon first performing the DAR under solvent conditions (toluene and *o*-dichlorobenzene). We then made attempts under forcing conditions (neat). However, it did not undergo cycloaddition with bitrindanylidine 7 perhaps due to the sterically bulkier size of the dienes.

DFT calculations

These interesting observations prompted us to study the selectivity of all the dienes (**D_1–D_6**) towards cycloaddition with 7 using Density Functional Theory (DFT) calculations. The structural optimization, molecular orbitals and vibrational frequency calculations were performed at the M06-2X/6-311++G(d, p) level using the Gaussian09 Software package.[21,22] The absolute value of the dihedral angle in 7 obtained from DFT studies is 177.38°. We have optimized all the cyclic and acyclic dienes such as 1,3-cyclopentadiene (**D_1**), 1,3-butadiene (**D_2**), isoprene (**D_3**), 6,6-dimethylfulvene (**D_4**), spiro[2.4]hepta-4,6-diene (**D_5**) and anthracene (**D_6**). The energy gap of the dienes is in ascending order as follows: **D_3** (2.164 eV) < **D_6** (2.168 eV) < **D_4** (2.796 eV) < **D_5** (3.664 eV) < **D_1** (3.743 eV) < **D_2** (3.891 eV).

The computed values for activation energy for all the cycloadducts are included in Table 1. The lowest value for Gibbs free energy is predicted for the isoprene adduct **10**, butadiene adduct **9** and butterflyene **8** (an adduct of 7 and cyclopentadiene **D_1**), which amounts to −19.435 kcal mol^{-1}, −16.444 kcal mol^{-1} and 3.346 kcal mol^{-1}, respectively. These values are lower than those of all the remaining cycloadducts of the dienes (**D_4–D_6**) which did not undergo cycloaddition.

These observations are in good agreement with the experimental results. We have also calculated the HOMO–LUMO gap of reactants, as it gives important parameters such as chemical potential (μ), global hardness (η), global electrophilicity index (ω), *etc*. These global parameters and frontier molecular orbit levels calculated are given in Table 2. The computed reaction energy diagram is shown in Fig. 6. The HOMO energy of tetracyanoethene (TCE) is −0.3486 au (−9.485 eV)[23] and it is used to compute the global nucleophilicity (N') of diene, which can be expressed as $N' = E_{HOMO(diene)} - E_{HOMO(TCE)}$.

Table 1 Change in Gibbs free energy, enthalpy, and entropy in kcal mol^{-1} at 298.15 K

Cycloadducts of dienes	Formation energy	ΔG	ΔH	ΔS
D_1	−0.733	3.346	−13.455	−0.056
D_2	−1.599	−16.444	−33.045	−0.056
D_3	−1.723	−19.435	−35.509	−0.054
D_4	−0.377	10.989	−6.126	−0.057
D_5	−0.350	12.259	−5.391	−0.059
D_6	−0.396	10.890	−6.262	−0.058

Table 2 The global parameters and frontier molecular orbit levels calculated at the M06-2X/6-311++G(d, p) level for the reactants

Diene/ dienophile	HOMO (eV)	LUMO (eV)	η (eV)	μ (eV)	$\omega = \mu^2/2\eta$ (eV)	$\Delta N_{max} = -\mu/\eta$	$N = 1/\omega$ (eV)	N'	$HOMO_{diene} - LUMO_{dienophile}$	$HOMO_{dienophile} - LUMO_{diene}$
$\mathbf{D_1}$	−7.535	−0.024	3.743	−3.779	1.908	1.010	0.524	1.950	−7.329	6.313
$\mathbf{D_2}$	−7.953	−0.085	3.891	−4.019	2.075	1.033	0.482	1.532	−7.747	6.252
$\mathbf{D_3}$	−6.515	−1.094	2.164	−3.804	3.344	1.758	0.299	2.970	−6.309	5.243
$\mathbf{D_4}$	−7.279	−0.843	2.796	−4.061	2.949	1.452	0.339	2.206	−7.073	5.494
$\mathbf{D_5}$	−7.343	−0.008	3.664	−3.675	1.844	1.003	0.542	2.142	−7.137	6.329
$\mathbf{D_6}$	−6.719	−1.192	2.168	−3.955	3.608	1.824	0.277	2.766	−6.513	5.145
7	−6.337	−0.206	2.963	−3.271	1.806	1.104	0.554			

Conclusions

In summary, we have imagined, retrosynthetically planned and executed the synthesis of an intricate molecular framework **8** that has a butterfly-like appearance. The role of steric interactions of the dienes butadiene $\mathbf{D_2}$ and isoprene $\mathbf{D_3}$ with 7 has also been investigated. The endgame of the synthesis consists of an unusual DAR on a tetrasubstituted double bond in a bicyclopentylidene moiety embedded in 7. The DAR favoured dienes $\mathbf{D_1}$–$\mathbf{D_3}$ from the less hindered face of 7, and in the case of the cyclic dienes $\mathbf{D_4}$–$\mathbf{D_6}$, steric considerations appear to decide the fate of the DAR. Theoretical calculations are also found to be in strong agreement with our experimental data for the dihedral angle in 7. It is discovered that the estimated Gibbs free energy of the cycloadducts of dienes $\mathbf{D_1}$–$\mathbf{D_3}$ is lower than that of the cycloadducts of dienes $\mathbf{D_4}$–$\mathbf{D_6}$, which is consistent with the experimental findings of the corresponding successful reactions.

Experimental

Synthesis of bitrindanylidine 7

Under an argon atmosphere, a three-neck pre-flamed dried round bottom flask equipped with a magnetic stirrer was charged with titanium tetrachloride (2.86 g, 15.08 mmol) and 30 ml of dry THF. The mixture was cooled to 0 °C. Then activated zinc dust (2.46 g, 37.71 mmol) was added slowly to the yellow suspension with the temperature being kept at 0 °C. The suspension then turned into dark brown immediately and was stirred for 15 min at 0 °C. The solution of trindan-1-one **6** (0.8 g, 3.77 mmol) in 30 ml of dry THF was added dropwise over a period of 0.5 h. After the addition, the reaction mixture was stirred at room temperature until **6** was consumed (monitored by TLC). The reaction was quenched with 10% aqueous sodium bicarbonate and taken up in ethyl acetate. The organic layer was collected and concentrated. The dark brown crude product was chromatographed on a column of silica gel using light petroleum to furnish 0.443 g of bitrindanylidine 7 as a white solid (mp 218 °C) in 30% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.92–2.72 (m, 23H), 2.20–2.02 (m, 8H), 1.56 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.24, 139.44, 139.19, 138.26, 137.76, 137.22, 135.78, 37.45, 34.69, 31.66, 31.40, 31.01, 30.56, 27.06, 25.56, 15.39; HRMS (EI): *m*/*z* calculated for $C_{30}H_{33}$ $[M + H]^+$: 393.2582, found 393.2581.

General method for the synthesis of carbocyclic adducts 8–10

A 50 ml three-neck round bottom flask equipped with a condenser and magnetic stirrer was kept under an inert argon atmosphere. In the RBF, bitrindanylidine 7 (100 mg, 0.25 mmol) was taken with/without 15 ml of dry toluene. Excess amounts of various dienes ($\mathbf{D_1}$–$\mathbf{D_3}$) were injected in the reaction mixture. The solution was then heated to reflux in an oil bath for several hours. After completion of the reaction (monitored by TLC), the solution was then removed under vacuum distillation and the residues were purified by column chromatography on silica gel using light petroleum as an eluent to afford cycloadducts **8–10**.

Butterflyene adduct 8. Bitrindanylidine 7 (100 mg, 0.25 mmol) in 10 ml of dicyclopentadiene was directly taken in a sealed tube. The reaction mixture was then heated up to 180 °C to generate cyclopentadiene *in situ*. After completion of the reaction (12 h), the solution was removed using vacuum distillation and the crude product was chromatographed with a column of silica gel using light petroleum to furnish 90 mg of the butterflyene adduct as a white solid (mp >320 °C) in 85% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.99 (s, 2H), 5.61 (d, J = 5.7 Hz, 1H), 5.44 (d, J = 5.6 Hz, 1H), 2.75 (s, 2H), 2.28 (d, J = 8.5 Hz, 3H), 2.20 (d, J = 17.5 Hz, 2H), 2.18–2.08 (m, 6H), 2.08–1.97 (m, 5H), 1.93 (dd, J = 16.3, 5.2 Hz, 3H), 1.90 (d, J = 4.7 Hz, 1H), 1.86 (dd, J = 19.3, 7.4 Hz, 2H), 1.68 (dd, J = 9.7, 4.9 Hz, 1H), 1.65–1.58 (m, 2H), 1.55 (s, 2H), 1.32–1.24 (m, 2H), 1.11 (t, J = 7.6 Hz, 2H), 0.94 (d, J = 10.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.22, 132.31, 131.16, 55.68, 54.03, 47.64, 47.35, 47.07, 46.59, 44.41, 44.13, 43.90, 43.79, 43.59, 41.25, 40.83, 40.75, 39.50, 39.43, 37.38, 31.67; HRMS (ESI): *m*/*z* calculated for $C_{35}H_{39}$ $[M + H]^+$: 459.3052, found 459.3050.

Butadiene adduct 9. Initially, butadiene sulfone (300 mg, 2.55 mmol) was taken in 15 ml of dry toluene and the reaction mixture was heated until 80 °C to form butadiene *in situ*. Then bitrindanylidine 7 (100 mg, 0.25 mmol) was added to the reaction mixture and then it was refluxed. A small amount of sulfolene was added portionwise during the course of the reaction. The reaction was completed after 4.5 h (TLC) and the solvent was removed under reduced pressure to give a yellow crude product. It was then purified by column chromatography on

silica gel using light petroleum as an eluent to furnish 90 mg of the butadiene adduct as a white solid (mp 232 °C) in 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 (s, 1H), 4.52 (d, J = 9.0 Hz, 1H), 3.31 (q, J = 6.9 Hz, 2H), 3.13 (d, J = 7.8 Hz, 2H), 2.97–2.81 (m, 14H), 2.65 (d, J = 7.5 Hz, 2H), 2.54 (dt, J = 12.4, 8.9 Hz, 1H), 2.22 (q, J = 5.2, 3.4 Hz, 2H), 2.10–1.97 (m, 2H), 1.58 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.36, 139.17, 138.83, 138.46, 138.24, 138.05, 137.51, 136.71, 134.10, 127.11, 43.70, 35.88, 34.06, 31.63, 31.31, 31.19, 31.02, 30.88, 30.81, 29.21, 25.93, 25.51, 25.46; HRMS (ESI): the molecular ion peak at 447.30 (M + 1) was not observed in HRMS maybe because the compound experienced a retro-Diels–Alder reaction during the analysis, and the peak displayed fragment ions at m/z 393.25 for $C_{30}H_{32}$.

Isoprene adduct 10. Bitrindanylidine **7** (100 mg, 0.25 mmol) in 15 ml of isoprene was taken in a sealed tube at 120 °C for 24 h. After completion of the reaction (TLC), the solvent was removed under reduced pressure and the remaining crude product was chromatographed using light petroleum as an eluent to furnish 102 mg of the isoprene adduct as a white solid (mp 258–260 °C) in 86% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.52 (s, 1H), 4.49 (d, J = 8.8 Hz, 1H), 2.85 (dq, J = 26.2, 7.4, 6.7 Hz, 30H), 2.14 (dt, J = 11.1, 7.3 Hz, 9H), 1.54 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.23, 139.42, 139.16, 138.93, 138.25, 138.09, 137.73, 137.61, 137.20, 136.81, 135.77, 134.20, 131.04, 127.18, 43.82, 37.44, 35.98, 34.67, 34.19, 31.75, 31.64, 31.40, 31.30, 31.13, 30.99, 30.92, 30.55, 29.32, 27.03, 26.01, 25.60, 25.54; HRMS (ESI): m/z calculated for $C_{35}H_{41}$ $[M + H]^+$: 461.3208, found 461.3208.

Conflicts of interest

There are no conflicts to declare.

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