

## Fused-Ring Systems | Hot Paper |

## Energetics of Formation of Cyclacenes from 2,3-Didehydroacenes and Implications for Astrochemistry

Divanshu Gupta,<sup>[a]</sup> Alain Omont,<sup>[b]</sup> and Holger F. Bettinger\*<sup>[a]</sup>

**Abstract:** The carriers of the diffuse interstellar bands (DIBs) are still largely unknown although polycyclic aromatic hydrocarbons, carbon chains, and fullerenes are likely candidates. A recent analysis of the properties of *n*-acenes of general formula  $C_{4n+2}H_{2n+4}$  suggested that these could be potential carriers of some DIBs. Dehydrogenation reactions of *n*-acenes after absorption of an interstellar UV photon may result in didehydroacenes. Here the reaction energies and barriers for formation of *n*-cyclacenes from 2,3-didehydroacenes (*n*-DDA) by intramolecular Diels–Alder reaction to dihydroetheno-cyclacenes (*n*-DEC) followed by ejection of ethyne by

retro-Diels–Alder reactions are analyzed using thermally assisted occupation density functional theory (TAO-DFT) for  $n=10$ –20. It is found that the barriers for each of the steps depend on the ring strain of the underlying *n*-cyclacene, and that the ring strain of *n*-DEC is about 75 % of that of the corresponding *n*-cyclacene. In each case, ethyne extrusion is the step with the highest energy barrier, but these barriers are smaller than CH bond dissociation energies, suggesting that formation of cyclacenes is an energetically conceivable fate of *n*-acenes after multiple absorption of UV photons.

## Introduction

Heilbronner proposed the hoop shaped structures of cyclacenes for the first time in 1954.<sup>[1]</sup> Cyclacenes are polycyclic compounds where *n* six membered benzene rings are fused together to form a belt-like structure (Figure 1). Such cyclacenes, sometimes called  $[6]_n$ cyclacenes to distinguish from  $[l,m]_n$ cyclacenes being composed of *l*- and *m*-membered carbon rings,<sup>[2]</sup> can be considered to be comprised of two peripheral circuits interconnected by rung bonds.<sup>[3]</sup> The peripheral rims of  $[6]_n$ cyclacenes, for the remainder of the paper simply named *n*-cyclacenes, are reminiscent of two transulenes, i.e., circular, all-*trans* cyclic polyene ribbons.<sup>[4–6]</sup>

The highly strained structures<sup>[7–9]</sup> of *n*-cyclacenes pose a formidable obstacle towards their syntheses, only leading to unsuccessful attempts in producing *n*-cyclacene.<sup>[2,3,7,10]</sup> Neverthe-

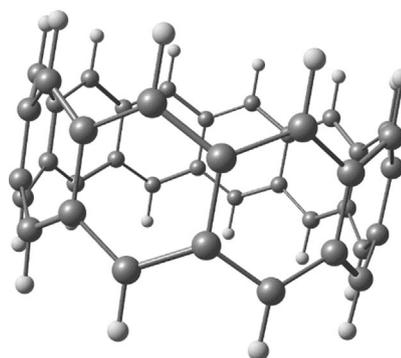


Figure 1. Structure of 10-cyclacene.

less, continuous efforts in order to prepare *n*-cyclacenes have made progress. Previous studies reported the synthesis of precursors and derivatives of *n*-cyclacenes, such as the seminal work towards [12]cyclacene by Stoddart et al.,<sup>[11–13]</sup> towards [8]cyclacene by Cory et al.,<sup>[14,15]</sup> and towards [18]cyclacene by Schlüter et al.<sup>[16,17]</sup> Recently, Itami et al. described the synthesis of [12], [16], and [24] carbon nanobelts that are composed of linearly and angularly fused sections.<sup>[18,19]</sup>

Cyclacenes of the general formula  $C_{4n}H_{2n}$  are closely related to acenes,  $C_{4n+2}H_{2n+4}$ , and are indistinguishable under cyclic boundary conditions in the infinite limit ( $n \rightarrow \infty$ ). It was recently suggested that polyacenes could be carriers of some diffuse interstellar bands (DIBs)<sup>[20]</sup> that originate as a result of absorption of light in the interstellar medium. More than 500 DIBs are known in the optical and near-infrared region of the electromagnetic spectrum.<sup>[21–23]</sup> The first DIBs have been known since 1922; however, most of the carrier molecules remain unidentified to date, but four bands were attributed to  $C_{60}^+$ .<sup>[24–27]</sup> Poly-

[a] D. Gupta, Prof. Dr. H. F. Bettinger  
Institut für Organische Chemie, Universität Tübingen  
Auf der Morgenstelle 18, 72076 Tübingen (Germany)  
E-mail: Holger.Bettinger@uni-tuebingen.de

[b] Prof. Dr. A. Omont  
Institut d'Astrophysique de Paris, Sorbonne Université  
UPMC Université Paris 6 and CNRS, UMR 7095  
98bis boulevard Arago, 75014 Paris (France)

Supporting information and the ORCID identification numbers for the authors of this article can be found under:  
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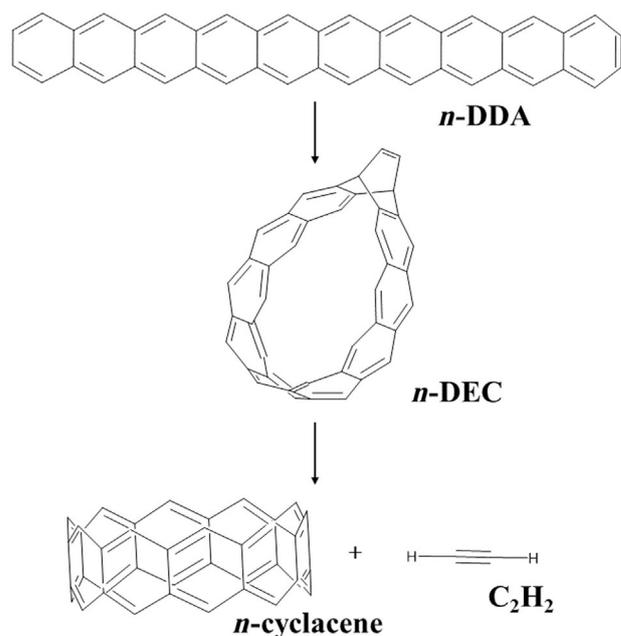
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cyclic aromatic hydrocarbons (PAHs) and other large carbon-bearing molecules are believed to be the best candidate carrier molecules of DIBs.<sup>[28–31]</sup>

Among PAHs, there are various arguments which make *n*-acenes good DIB carrier candidates.<sup>[20]</sup> Their expected regular series of very strong visible bands from  $n \approx 11$  to  $\approx 16$ –18 match the main wavelength domain of DIBs ( $\approx 4000$ – $7500$  Å). For such *n* values they are just stable against interstellar UV photodissociation in diffuse and translucent interstellar clouds where DIBs are formed. The correlation of their band wavelength and their photostability with their length could explain the general correlation observed between the DIB wavelength and the apparent UV resilience of their carriers.<sup>[20,32]</sup> However, the lower thermodynamic stability of polyacenes compared to other PAHs remains a major question for their interstellar abundance, and some processes allowing a substantial abundance, e.g., through reactions with abundant  $C^+$  and O, would need to be identified. For the smallest values of *n*, the first products of interstellar UV photodissociation of *n*-acenes should be partially dehydrogenated acenes resulting from the successive photocleavage of their weakest CH bonds.<sup>[20]</sup>

As for a given *n* the difference in formula of acenes and cyclacenes is  $C_2H_4$ , ejection of two hydrogen atoms from acenes followed by loss of acetylene,  $C_2H_2$ , could provide a mechanism for transformation of acenes to cyclacenes in interstellar space, making cyclacenes interesting candidates for DIB carriers. We have shown previously by computational means that the CH bonds at the terminal rings are the weakest in large acenes.<sup>[20]</sup> Twofold dehydrogenation at the terminal rings by successive absorption of two UV photons in the interstellar medium is expected to be most facile under a critical value of  $n_{cr} \approx 12$ –13 and result in 2,3-didehydroacenes (*n*-DDA). The unsaturated edge of the acene resembles an aryne, a highly reactive intermediate with high versatility in synthetic organic chemistry.<sup>[33–37]</sup> A fundamental reaction of arynes is the  $[\pi 4s + \pi 2s]$  cycloaddition with dienes,<sup>[38]</sup> the Diels–Alder reaction, and it is well-known that acenes can serve as dienes in Diels–Alder reactions with arynes.<sup>[39,40]</sup> In this paper we analyze computationally the transformation of *n*-DDA into cyclacenes by Diels–Alder reaction to dihydro-etheno-cyclacenes (*n*-DEC) followed by ejection of acetylene in a retro-Diels–Alder reaction (Figure 2).

So far, knowledge of *n*-cyclacene properties is based on theoretical calculations. The unusual electronic and magnetic properties predicted by computational analyses and the structural resemblance to carbon nanotubes have created interest in studying structure-property relationship of *n*-cyclacenes for several decades.<sup>[3,8,41–48]</sup> Accurate prediction of the properties of *n*-cyclacenes is challenging for traditional electronic structure methods due to the presence of strong static correlation effects.<sup>[49]</sup> For systems with strong static correlation effects,<sup>[50]</sup> Kohn–Sham density functional theory (KS-DFT)<sup>[51]</sup> with conventional (i.e., semilocal, hybrid, and double-hybrid) exchange–correlation (XC) density functionals can yield unreliable results in the case of spin-restricted or suffer from spin contamination for spin-unrestricted (or spin-polarized) KS-DFT as shown for the closely related acene series.<sup>[52–59]</sup> High-level ab initio multi-



**Figure 2.** Mechanism of formation of a *n*-cyclacene from a *n*-didehydroacene (*n*-DDA) involving the *n*-dihydro-etheno-cyclacene (*n*-DEC) as intermediate studied in this work. In the present example  $n = 10$ .

reference methods are typically required to accurately predict the properties of systems with strong static correlation effects.<sup>[49,60–65]</sup> There have been very few studies on the properties of larger *n*-cyclacenes using multi-reference methods, because the active spaces either quickly reach intractable sizes for larger systems or their proper choice causes problems.<sup>[8,55,66,67]</sup>

To overcome the computational expense of high-level ab initio multi-reference methods, thermally assisted-occupation density functional theory (TAO-DFT) was recently developed,<sup>[57,58]</sup> and shows to be a very efficient electronic structure method for studying the properties of large ground-state systems (e.g., containing up to a few thousand electrons) with strong static correlation effects.<sup>[52,68,69]</sup> TAO-DFT is a density functional theory with fractional orbital occupations, wherein strong static correlation is explicitly described by the entropy contribution,<sup>[57]</sup> with a function of the fictitious temperature and orbital occupation numbers. The entropy contribution in TAO-DFT, just like the static correlation energy of a system, is always nonpositive and is insignificant for a single-reference (SR) system and can significantly lower the total energy of a multi-reference (MR) system. Accordingly, TAO-DFT reduces to KS-DFT for SR systems, and outperforms KS-DFT for MR systems. TAO-DFT has been widely applied to study the electronic properties of various MR systems at the nanoscale level including acenes and cyclacenes<sup>[52–54,68–70]</sup> due to its computational efficiency that is similar to KS-DFT. Therefore, we adopt TAO-DFT to investigate the possibility of *n*-cyclacene ( $n = 10$ – $20$ ) formation from the corresponding *n*-didehydroacene.

## Computational details

We performed all TAO-DFT calculations with Q-Chem 5.2,<sup>[71]</sup> acquiring the numerical grid containing 75 radial points in the Euler–Maclaurin quadrature and 302 angular points in the Lebedev grid. Structures were fully optimized with TAO-LDA adopting the 6-31G(d) basis set. TAO-LDA is TAO-DFT with the LDA XC density functional and the LDA  $\theta$ -dependent density functional  $E_{\theta}^{\text{LDA}}$ <sup>[57]</sup> with the fictitious temperature  $\theta=7$  mhartree.<sup>[57]</sup> In addition, the general gradient approximation (GGA) functional introduced by Perdew, Burke, and Ernzerhof (PBE) in its TAO implementation was employed in this study.<sup>[58]</sup> The structures of the lowest energy singlet and triplet states of *n*-DDA, *n*-cyclacene, and *n*-DEC ( $n=10$ – $20$ ) as well as the transition states for the intramolecular Diels–Alder reactions of didehydroacenes and the elimination of acetylene from *n*-DEC to form cyclacenes and acetylene by retro Diels–Alder reaction for  $n=10$ , 15, and 20 were fully optimized by performing TAO-LDA calculations. The TAO-LDA data we obtained for cyclacenes and acenes were identical to those reported previously.<sup>[53, 57, 58]</sup> The TAO-LDA geometries were used for subsequent TAO-PBE/6-31G(d) single point computations, TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d), as this level is expected to give a better estimate for reaction barriers and reaction energies based on our benchmark calculations. The singlet energies computed with spin-unrestricted TAO-DFT (LDA and PBE) were found to be numerically identical to the corresponding energies obtained from the spin-restricted treatment, implying that our calculations based on spin-unrestricted formalism do not lead to unphysical symmetry-breaking solutions, as reported previously for acenes and cyclacenes.<sup>[53, 57, 58]</sup>

For the benchmark calculations involving reactions of anthracene and pentacene, geometries were computed with the B3LYP<sup>[72, 73]</sup> functional in conjunction with Dunning's<sup>[74]</sup> correlation consistent triple- $\zeta$  basis set. These computations were performed using Gaussian 16.<sup>[75]</sup> Single point calculations based on the B3LYP/cc-pVTZ and TAO-LDA/6-31G(d) structures were performed using domain based local pair natural orbital (DLPNO) coupled cluster theory with single, double, and a perturbative estimate of triple excitation (DLPNO-CCSD(T)).<sup>[76–78]</sup> The DLPNO-CCSD(T) computations used the default parameters as implemented in ORCA 4.0<sup>[79]</sup> and the frozen core approximation. TightPNO cutoff is also employed with DLPNO-CCSD(T) for increased accuracy. These results are taken as reference for comparison with the TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) energies of the same systems.

## Results and Discussion

### Benchmark calculations

To examine the reliability of the TAO-DFT treatment compared to the gold standard of quantum chemistry, CCSD(T), we carried out benchmark calculations. In contrast to the actual systems of interest, the benchmark calculations were performed for smaller systems mimicking the chemical transformations studied. As the possible formation of cyclacenes involves cycloaddition of aryne and cycloreversion of acetylene, we chose the related cycloaddition of benzyne to the 1,4 and 9,10 positions of anthracene, and the acetylene cycloreversion from two etheno-bridged anthracene and three etheno-bridged pentacene isomers. The reaction of acetylene with acenes was studied computationally earlier.<sup>[80]</sup> As even for these smaller model reactions CCSD(T) theory is computationally very demanding, we employed the domain based local pair natural orbital

(DLPNO) approximation<sup>[77, 81]</sup> to the canonical CCSD(T) result. A recent comprehensive evaluation showed very good agreement between DLPNO and canonical CCSD(T).<sup>[82]</sup> Although the degree of static correlation grows with length in the acene series, the smaller members anthracene and pentacene can be described by CCSD(T) despite shortcomings of the CCSD wavefunction.<sup>[83, 84]</sup>

For the benchmark evaluations two sets of geometries were employed in DLPNO-CCSD(T) single point energy computations, namely B3LYP/cc-pVTZ and TAO-LDA/6-31G(d). The former hybrid-DFT method is well-known to generally produce reliable geometries. The barrier heights and relative energies of the compounds for both sets of geometries are very similar (Figure 3). In only one instance, the difference was larger than 0.1 eV. Hence, the structures obtained from both B3LYP/cc-pVTZ and TAO-LDA/6-31G(d) are of similar quality with respect to the evaluation of reaction barriers and energies. Thus, the much more economical TAO-LDA functional is employed in the present study for geometry optimization.

The TAO-LDA energies, however, are in poor agreement with the DLPNO-CCSD(T) data (Figure 3). As expected, the LDA functional underestimates reaction barriers significantly. Compared to LDA, general gradient approximation (GGA) functionals, for example, PBE, generally underestimate the energy barriers less. We have refined the reaction energies and barriers by using TAO-PBE single point computations based on the TAO-LDA structures. Compared to DLPNO-CCSD(T) this much more economical approach gives reaction barriers that are too low by about 0.3 eV or less. Hence, the TAO-PBE//TAO-LDA model chemistry seems attractive for studying the title reactions as the obtained barriers are expected to be overall too low, but only by a small margin of a few tenth of an electron volt.

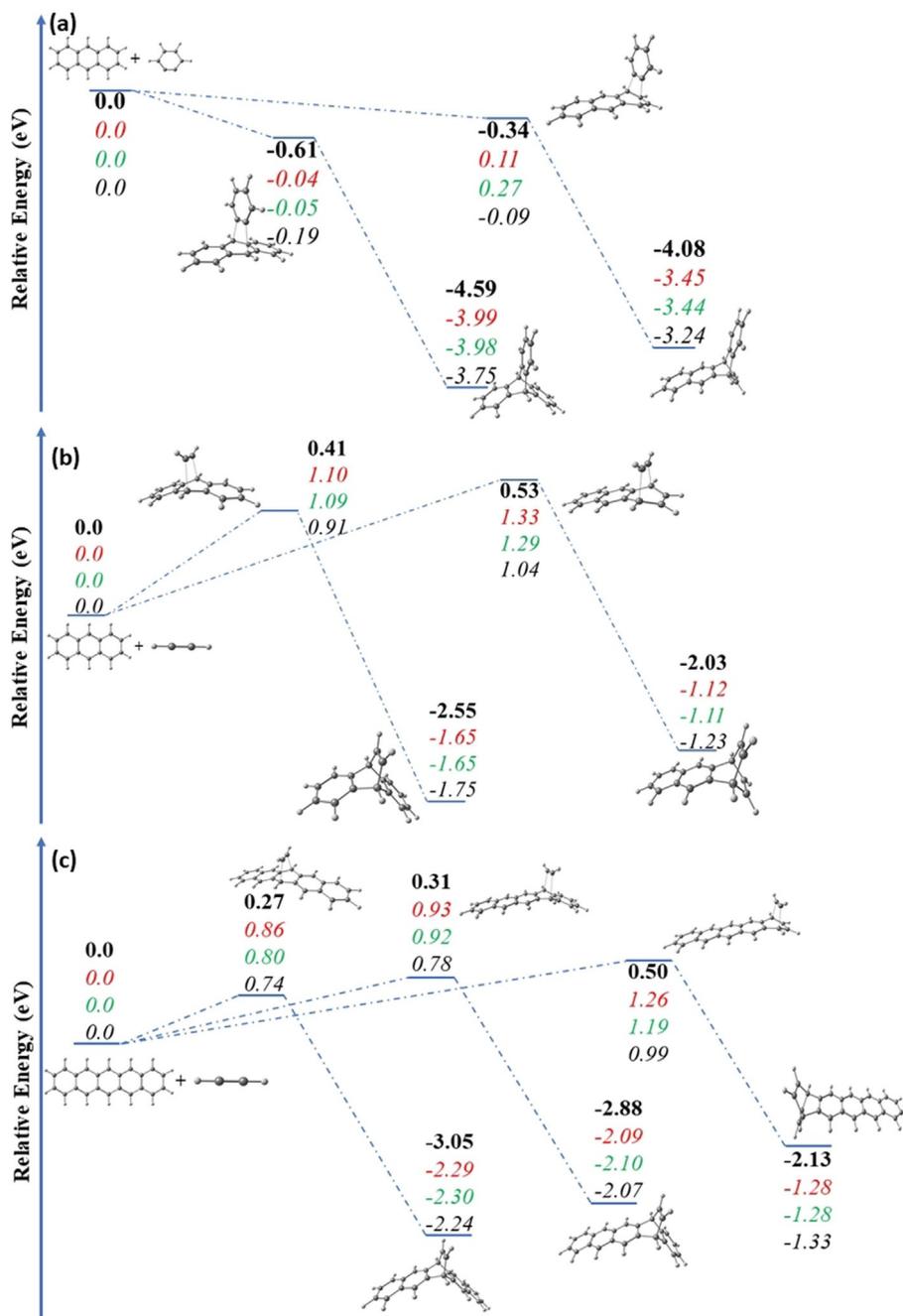
### Singlet–triplet energy gap

The singlet–triplet energy gaps of acenes and cyclacenes were studied previously with many different methods,<sup>[60, 84, 85]</sup> including TAO-LDA/6-31G(d).<sup>[53]</sup> To determine the spin multiplicity of the electronic ground state of *n*-DDA and *n*-DEC ( $n=10$ – $20$ ), we performed calculations based on spin-unrestricted TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d). The lowest energy singlet and triplet states of *n*-DDA and *n*-DEC were obtained, with the corresponding geometries being completely relaxed. Subsequently, we calculated the singlet–triplet energy gap  $E_{\text{ST}}$  of *n*-DDA and *n*-DEC as in Equation (1):

$$E_{\text{ST}} = E_{\text{T}} - E_{\text{S}} \quad (1)$$

with  $E_{\text{T}}$  and  $E_{\text{S}}$  being the lowest triplet and lowest singlet energies, respectively (see Figure 4, Table S1).

The oscillatory behavior of the  $E_{\text{ST}}$  values with *n*-cyclacene size (see Figure 4) has been observed and discussed before in the context of the cryptoannulenic effect.<sup>[3, 43, 44, 53]</sup> This is due to the nature of peripheral circuits of cyclacenes which influence the molecular orbital characteristics. These peripheral circuits are of two types, 4k and 4k+2 (where k is an integer), depend-



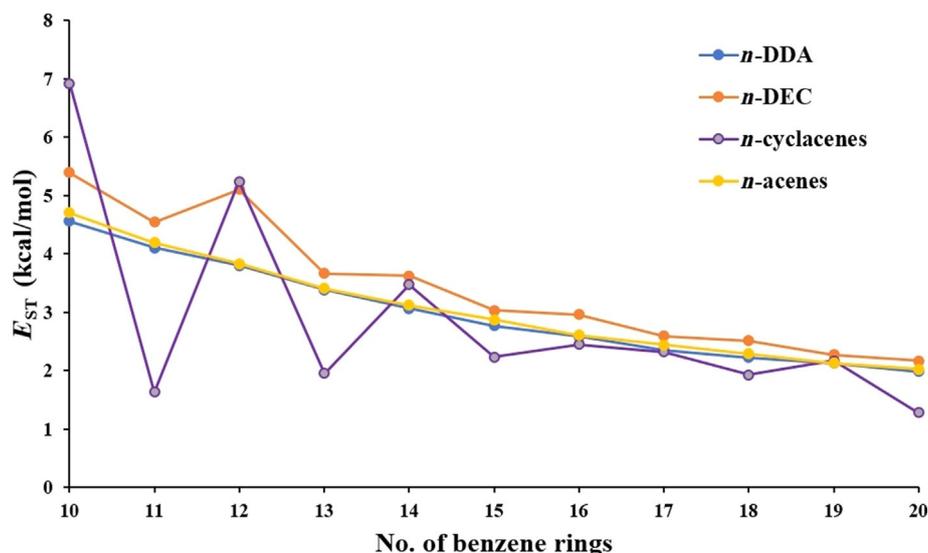
**Figure 3.** Reaction Pathways of (a) benzyne addition in anthracene (b) acetylene addition in anthracene and (c) acetylene addition in pentacene in eV (Bold; TAO-LDA/6-31G(d); Red: DLPNO-CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ; Green: DLPNO-CCSD(T)/cc-pVTZ//TAO-LDA/6-31G(d); Italics: TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d)).

ing upon the number of benzene rings in the  $n$ -cyclacene. Previous studies show that  $n$ -cyclacenes with an even-number of benzene rings (4k type) are thermodynamically more stable than that with odd-number of benzene rings (4k+2 type) for  $n \leq 10$ , but this difference is attenuated quickly with increasing size.<sup>[3,43–45]</sup> The oscillatory amplitudes of the  $E_{ST}$  values are significantly damped in the  $n$ -DEC series as the cryptoannulenic effect is significantly reduced (Figure 4). The  $E_{ST}$  values of  $n$ -DDA decrease monotonically, and are close to those of acenes at the same level of theory.<sup>[57]</sup> This is a consequence of the

$\pi/\pi^*$  nature of the frontier orbitals of  $n$ -DDA and contrasts parent benzyne with its in-plane frontier orbitals.

### Strain energy of cyclacenes

The strain energies (SE) of highly strained molecules have significant impact on their stability and reactivity, thereby affecting the feasibility of synthesis of these molecules either in the laboratory or in interstellar space.<sup>[86]</sup> The SE of cyclacenes was evaluated before by Sadowsky et al.<sup>[49]</sup> and Segawa et al.<sup>[9]</sup>



**Figure 4.** Singlet-triplet energy gap ( $E_{ST}$ ) of *n*-DDA, *n*-cyclacene, *n*-DEC and *n*-acenes as a function of the number *n* of benzene rings, calculated at the TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) level of theory.

using the UM06-L and RB3LYP functionals, respectively, and the 6-31G(d) basis set. Both groups determined the strain using the method that was applied by Hopf and co-workers for calculating the SE of [*n*]circulenes.<sup>[87]</sup> Fitting a linear function to the plot of the normalized energy of the ( $C_4H_2$ ) unit, i.e., energy of the *n*-cyclacene divided by *n*, versus  $n^{-2}$  gives the energy  $E_{(C_4H_2)}$  of a strain-free  $C_4H_2$  fragment as intercept. The strain of a *n*-cyclacene is then the difference of its total energy and *n*-times the number of strain-free  $C_4H_2$  fragments [Eq. (2)]:

$$E_{\text{strain}} = E_{\text{cyclacene}} - n \times E_{(C_4H_2)} \quad (2)$$

At the TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) level of theory, the strain energy analysis gives  $E(n\text{-cyclacene}) \times n^{-1} = 1231.4 \times n^{-2} - 96287 \text{ kcal mol}^{-1}$  with a very good correlation ( $R^2 = 0.9973$ , Figure 5a and 5b). The energy of the unstrained  $C_4H_2$  fragment is thus  $96287 \text{ kcal mol}^{-1}$ , while  $1231.4 \times n^{-2} \text{ kcal mol}^{-1}$  is the SE of the  $C_4H_2$  repeat unit in a *n*-cyclacene. Thus, the SE of a *n*-cyclacene can be determined as  $1231.4 \times n^{-1} \text{ kcal mol}^{-1}$  (Figure 5c). Our strain energy per  $C_4H_2$  unit,  $1231.4 \times n^{-2} \text{ kcal mol}^{-1}$ , is in-between the values obtained previously ( $1324.3 \times n^{-2}$  by Segawa et al.<sup>[9]</sup> and  $1175.9 \times n^{-2}$  derived from the data reported in Table 2 of Sadowsky et al.<sup>[49]</sup>).

The alternative approach for estimation of SE using hypothetical homodesmotic reactions<sup>[88]</sup> was resulting in unphysical strain in the infinite limit according to Segawa et al.<sup>[9,89]</sup> We chose a homodesmotic equation (Figure 6) to calculate the SE, wherein the heat of reaction ( $\Delta E \text{ (kcal mol}^{-1})$ ) was plotted as a function of  $n^{-1}$  (Figure 7).

The linear fit to the data was of good quality ( $R^2 = 0.9927$ ) and gives a strain energy of  $1227.9 \times n^{-1} + 1.3194 \text{ kcal mol}^{-1}$  for a *n*-cyclacene (Figure 7). The extrapolation does not run through the origin, but the abscissa value is much smaller than the actual energy values in the  $n^{-1}$  range of 0.05 to 0.1 and we thus consider the deviation as numerical noise. The strain

energy obtained from the homodesmotic reaction (Figure 6),  $1227.9 \times n^{-1} + 1.3194 \text{ kcal mol}^{-1}$ , and by extrapolation of total energies,  $1231.4 \times n^{-1}$ , for a *n*-cyclacene are in reasonably good agreement (Figure 5c) considering that two different methods were employed for the derivation.

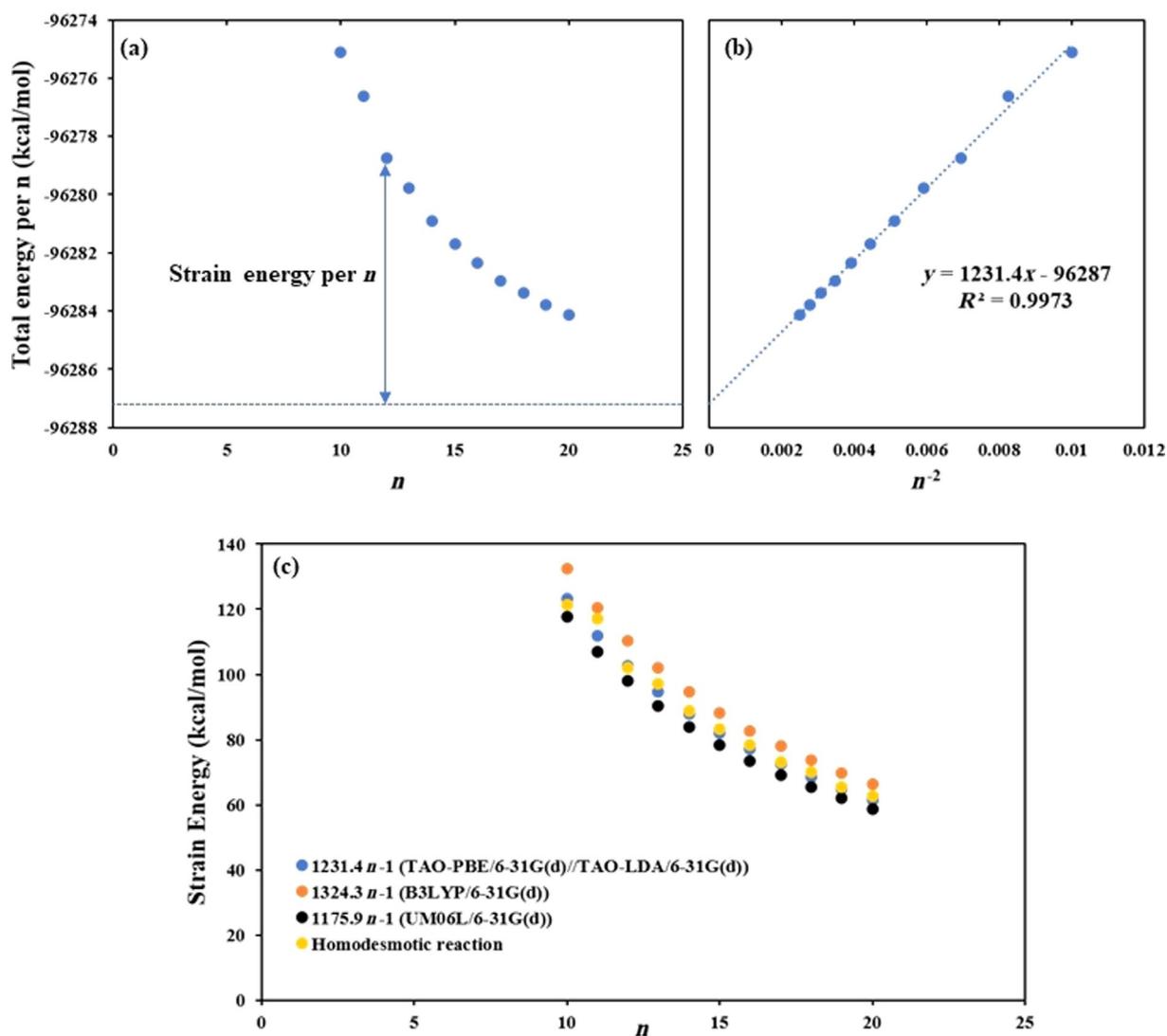
As an extrapolation of total energies is not readily possible for evaluation of the SE of *n*-DEC, it was determined using a homodesmotic equation (Figure 8). A linear fit to the data (Figure 9) gives a strain energy for *n*-DEC of  $982.69 \times n^{-1} - 3.4132 \text{ kcal mol}^{-1}$ . This shows that the strain of *n*-DEC is roughly 75% of the strain in the corresponding cyclacene.

### Cyclization of *n*-didehydroacenes (*n*-DDA)

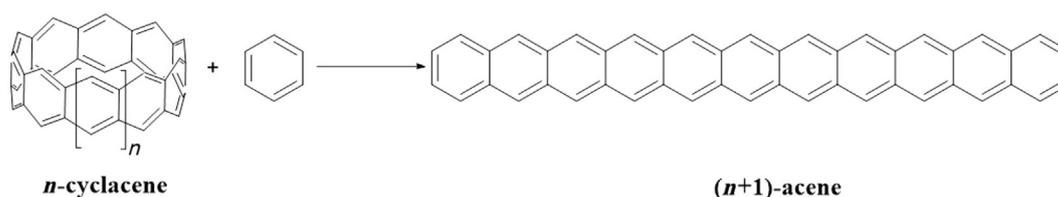
The results obtained at the TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) level show that the cyclization of *n*-DDA by Diels–Alder reaction into *n*-DEC is endothermic for smaller *n* ( $n = 10$ – $11$ ) and exothermic for  $n \geq 12$  (Figure 10). The energy of reaction increases monotonically with system size from 0.65 eV to  $-1.37 \text{ eV}$  on varying *n* from 10–20 for singlets and from 0.69 eV to  $-1.36 \text{ eV}$  for triplets, respectively. It is remarkable that the reactions are exothermic for  $n \geq 12$  and only slightly unfavorable for  $n = 10$ – $11$  despite the expected strain of the *n*-DEC products (vide infra). It appears that for  $n = 12$  the exothermicity of the Diels–Alder reaction ( $-3.2 \text{ eV}$  for the addition of benzyne to the 1,4-positions of anthracene, see Figure 3a) and the strain energy of the *n*-DEC (3.4 eV) balance each other.

The transition states for the intramolecular Diels–Alder reactions of *n*-DDA were computed for  $n = 10$ , 15, and 20 at the TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) level of theory (Figure 11). In all TSs there are two pairs of C–C bonds forming, but the degree of bond formation is not synchronous. The C–C distances differ in length and the differences increase from  $n = 20$  (0.004 Å), to  $n = 15$  (0.051 Å), and to  $n = 10$  ( $n = 0.244 \text{ Å}$ ).

The reaction of didehydroicosacene ( $n = 20$ ) has the largest exothermicity ( $-1.37 \text{ eV}$ ) and the smallest energy barrier



**Figure 5.** a) Total energy per number of repeat units ( $n$ ) of cyclacenes as a function of  $n$ . b) Total energy per number of repeat units ( $n$ ) of cyclacenes as a function of  $n^{-2}$  with a linear regression line. c) SEs of cyclacenes obtained by various computational methods [● at TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d), this work; ● at B3LYP/6-31G(d);<sup>[9]</sup> ● at UM06L/6-31G(d)<sup>[49]</sup>] and by (●) homodesmotic reaction (this work).



**Figure 6.** Homodesmotic reaction for  $n$ -cyclacene.

(1.67 eV) while that of didehydrodecacene ( $n=10$ ) has the highest endothermicity (0.65 eV) and the largest energy barrier (3.46 eV). For didehydropentadecacene ( $n=15$ ), the exothermicity (−0.69 eV) and energy barrier (2.28 eV) have intermediate values. From this trend, it is safe to extrapolate and summarize that along the series of  $n$ -DDA from  $n=10$  to  $n=20$ , the activation barriers for the cyclization by Diels–Alder reaction decreases with the increase in the number of benzene

rings. A more quantitative analysis reveals that the barrier height for all three cases studied,  $n=10$ , 15, 20, amounts to 84.2%, 84.8%, and 84.2%, respectively, of the strain energy of the forming  $n$ -DEC. It is thus possible to estimate the barriers for formation of other  $n$ -DEC as roughly 63% ( $0.75 \times 0.84$ ) of the strain energy of the parent  $n$ -cyclacene.

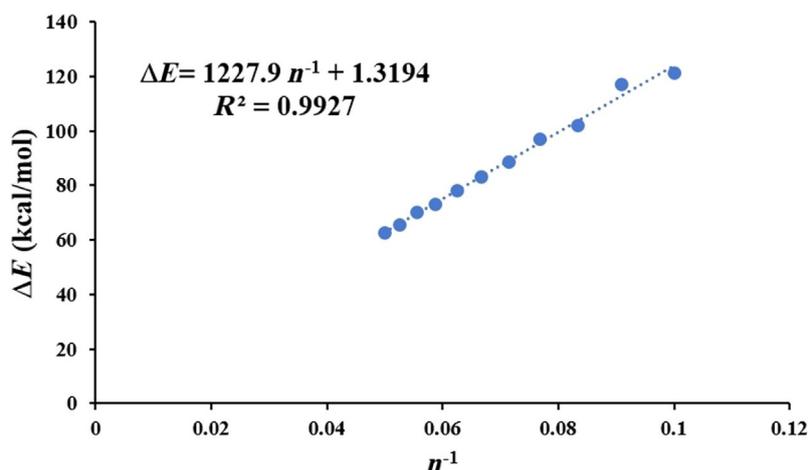


Figure 7. Reaction energy ( $\Delta E$ ) of the homodesmotic reaction of Figure 6 as a function of  $n^{-1}$ .

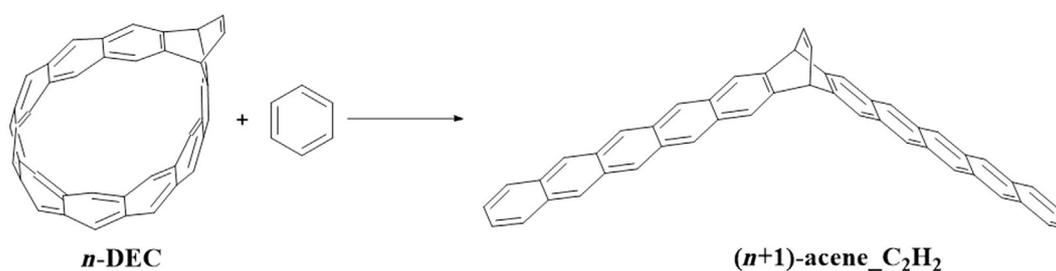


Figure 8. Homodesmotic reaction for  $n$ -DEC.

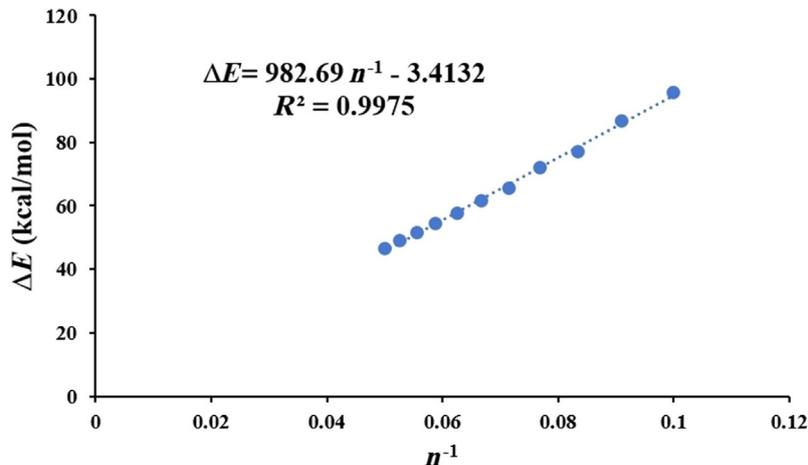


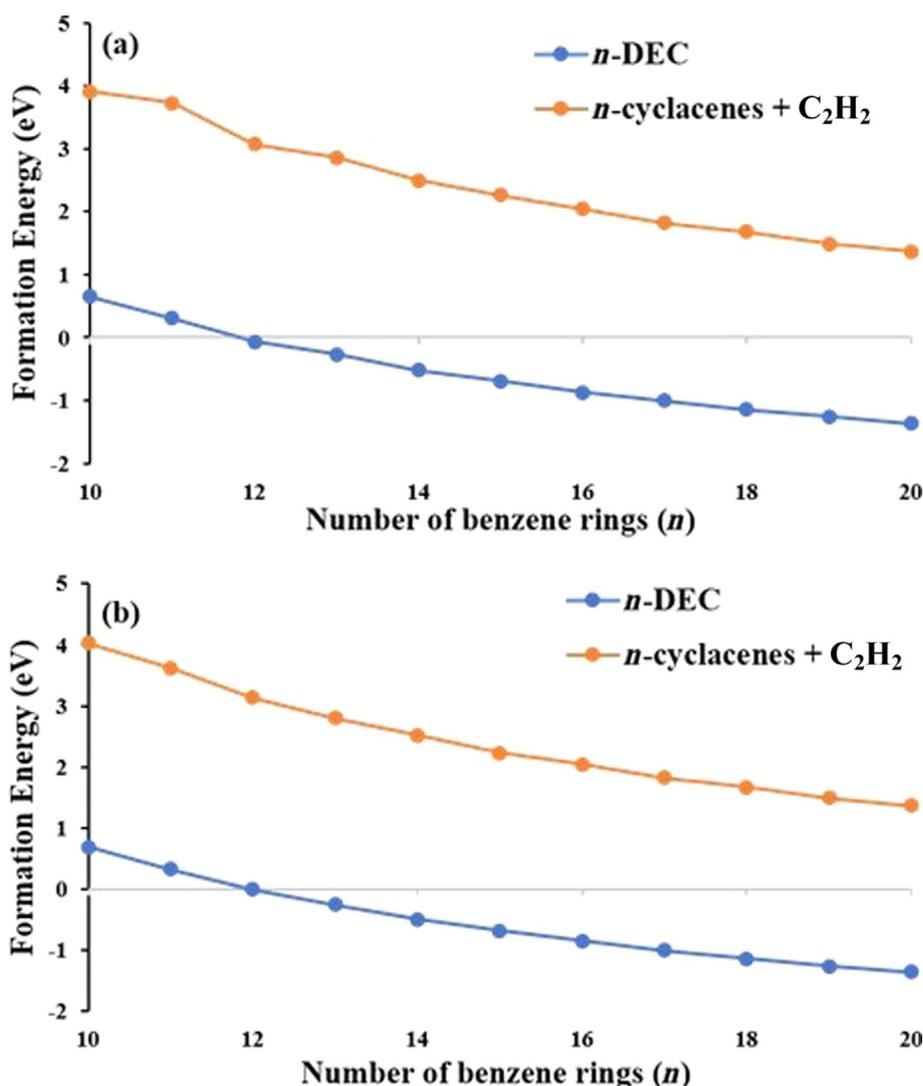
Figure 9. Reaction energy ( $\Delta E$ ) homodesmotic reaction of Figure 8 as a function of  $n^{-1}$ .

### Formation of cyclacenes by cycloreversion of $C_2H_2$

The final step of the proposed reaction sequence is the loss of  $C_2H_2$  which should proceed as a retro-Diels–Alder reaction. To the best of our knowledge, this reaction was not investigated before for cyclacenes, but computational data is available for acenes.<sup>[80]</sup> The loss of acetylene and formation of  $n$ -cyclacene from  $n$ -DEC is an energetically unfavorable process by 3.26 eV to 2.74 eV with increasing  $n$  from 10 to 20. Based on the

energy of  $n$ -DDA the formation of cyclacenes ranges from 3.91 eV to 1.37 eV and 4.02 eV to 1.36 eV for singlet and triplet states, respectively, on varying  $n$  from 10 to 20.

The transition states for the elimination of acetylene from  $n$ -DEC to form cyclacenes and acetylene by retro Diels–Alder reaction are structurally symmetric for  $n=10, 15,$  and  $20$  at the TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) level of theory (Figure 12) within numerical accuracy. Hence, the breaking of



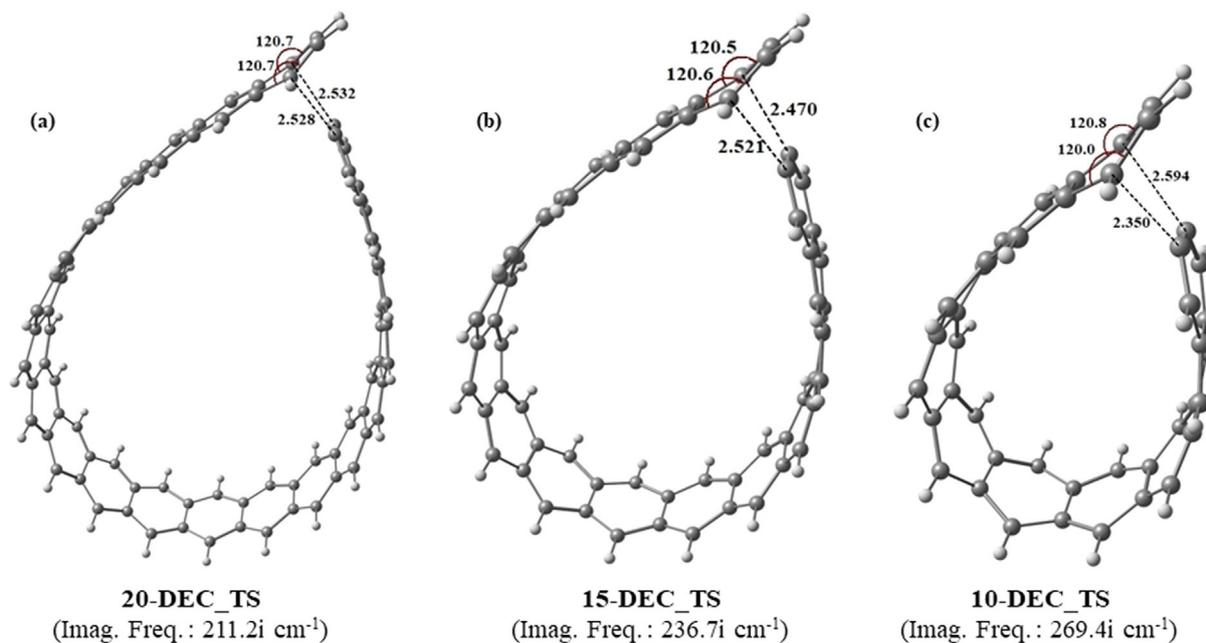
**Figure 10.** Formation energy of (a) singlets and (b) triplets of  $n$ -cyclacene and  $n$ -DEC from  $n$ -DDA as a function of the number of benzene rings, calculated using TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) level of theory.

the two C–C bonds occurs in an essentially synchronous process.

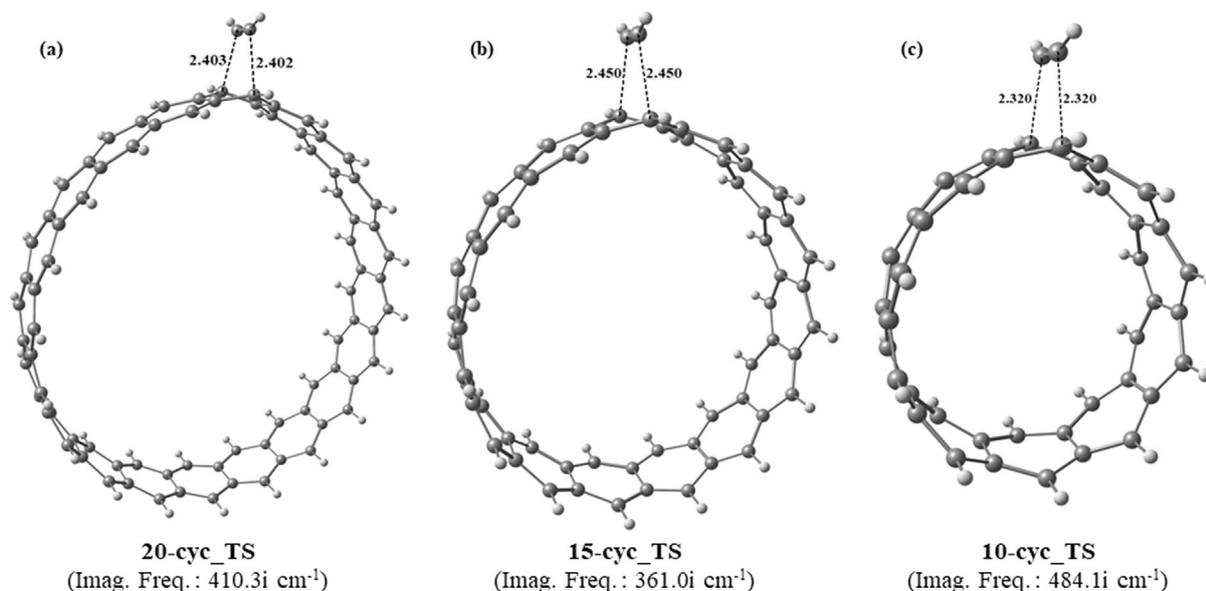
Further, the trend of reaction energy and barrier height in the retro-Diels–Alder reaction follows that of cyclization of  $n$ -DDA (Figure 10). The reaction of 20-DEC is most favorable (2.74 eV) and has the lowest energy barrier (3.11 eV), while the reaction of 10-DEC ( $n=10$ ) is least favorable (3.26 eV) and has the highest energy barrier (3.72 eV). For 15-DEC ( $n=15$ ), the reaction energy (2.95 eV) and energy barrier (3.34 eV) have intermediate values. Hence in this case it can as well be extrapolated and summarized that along the series of  $n$ -DEC from  $n=10$  to  $n=20$ , the activation barriers for the elimination of acetylene from  $n$ -DEC by retro Diels–Alder reaction decreases with the increase in the number of benzene rings. The potential energy surface outlined for the two-step transformation of  $n$ -DDA to cyclacenes and acetylene (Figure 13) follow overall the trend expected based on strain arguments. The larger the dihydroacene the more favorable is either of the steps.

#### Relevance for astrochemistry

As stated above,  $n$ -acenes could be good carrier candidates for the diffuse interstellar bands (DIBs) provided that they are abundant enough.<sup>[20]</sup> Moreover, dihydroacenes should be the first products of their interstellar UV photodissociation, and in diffuse interstellar clouds where DIBs are formed,  $n$ -DDA should be efficiently produced for  $n$  values smaller than a critical value  $n_{cr} \approx 12$ –13.<sup>[20]</sup> After their formation, the most probable process occurring to  $n$ -DDA is by far absorption of an interstellar UV photon with energy  $E_{UV} \approx 10$ –13.6 eV, which takes place about every few months. It should trigger cyclization by forming  $n$ -DEC, since this absorption raises the vibrational temperature to about 1000 K (see Appendix B in ref. [32]) and the barrier,  $E(n\text{-DEC}_{TS}) \approx 2.5$ –3.5 eV for  $n \approx 10$ –14 (Figure 13), is substantially smaller than the binding energy of the H atoms,  $E_H \approx 4.8$ –5.6 eV.<sup>[20]</sup> Immediately after this cyclization, the total energy above the ground level of  $n$ -DEC is  $E_{UV} - E(n\text{-DEC}) \approx 11$ –15 eV. This is enough for overcoming the activation energy



**Figure 11.** Optimized TSs of the cyclization reactions of *n*-DDA with selected structural parameters (in Å and degrees) and their respective imaginary frequency at TAO-LDA/6-31G(d).



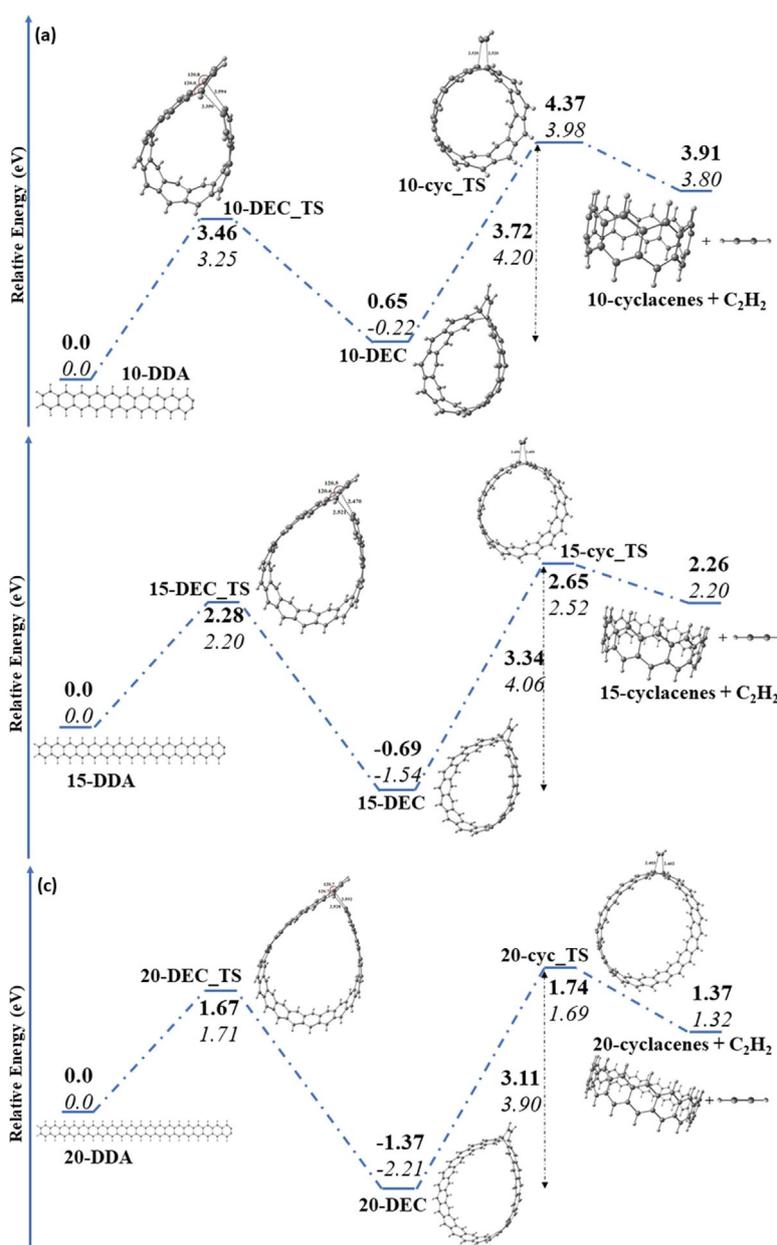
**Figure 12.** Optimized TSs of the elimination reaction of acetylene with selected interatomic distances (in Å) and their respective imaginary frequency at TAO-LDA/6-31G(d).

≈ 4.0–4.3 eV for the ejection of C<sub>2</sub>H<sub>2</sub> prior to infrared emission or ejection of an H atom whose activation energy, ≥ 4.8–5.6 eV, is significantly higher. A key point is that the formation of cyclacenes should practically be an irreversible process in the interstellar space because of the low abundance of small C<sub>*n*</sub>H<sub>*m*</sub> molecules, including C<sub>2</sub>H<sub>2</sub>, in diffuse interstellar clouds.<sup>[90]</sup>

The conclusion is that *n*-acenes for *n* ≤ 12–13 should be totally converted into cyclacenes in diffuse interstellar clouds. The same should be true for their cations, either because a

similar cyclization process is also efficient for *n*-acene cations, or because of the frequent changes of ionization state of interstellar PAHs. Cyclacenes and their cations with *n* ≤ 12–13 could therefore be considered as possible candidates for DIB carriers.

The situation is less clear for heavier acenes with *n* ≥ 14. Efficient interstellar cyclization might perhaps extend to higher values of *n* ≈ 14–16 if there was the possibility of formation of radical dehydroacenes from superhydrogenated acenes and



**Figure 13.** Reaction path for the cyclization of (a) didehydrodecacene (b) didehydropentadecacene and (c) didehydroicosacene leading to their respective cyclacenes (Bold: TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d); Italics: TAO-LDA/6-31G(d)).

photo-ejection of H<sub>2</sub>, followed by photo-formation of (DDA). However, the complexity of photoprocessing superhydrogenated acenes is such (e.g. ref. [91,92]) that it is impossible to conclude whether interstellar formation of *n*-cyclacenes could be efficient for  $n \approx 14$ –16 so that *n*-cyclacenes could coexist with *n*-acenes or even replace them.

## Conclusions

The investigation of *n*-DDA assumed to be formed from putative interstellar *n*-acenes by interstellar UV photodissociation and *n*-cyclacenes along with the transition states for their interconversion by ethyne extrusion with TAO-DFT allows to draw a number of conclusions for  $n = 10$ –20:

- 1) The electronic structure of 2,3-didehydroacenes (*n*-DDA) is quite similar to that of the parent *n*-acenes as evidenced by the very similar singlet-triplet energy splitting. It can thus be expected that some of their properties, e.g., optical spectra, resemble each other.
- 2) The didehydro-etheno-cyclacenes (*n*-DEC) have singlet-triplet energy gaps that are very similar to those of *n*-acenes and *n*-DDA, but are larger than those of *n*-cyclacenes, in particular those with odd *n*.
- 3) Two alternative methods for estimation of the strain energies of *n*-cyclacenes at the TAO-PBE/6-31G(d)//TAO-LDA/6-31G(d) level of theory, extrapolation of total energies ( $SE = 1231.4 \times n^{-1} \text{ kcal mol}^{-1}$ ) and homodesmotic reaction ( $SE = 1227.9 \times n^{-1} + 1.3194 \text{ kcal mol}^{-1}$ ), give quite similar values.

- 4) The strain energies of *n*-DEC are only about 75% of those of the corresponding *n*-cylacenes based on a related homodesmotic reaction.
- 5) As the addition of benzyne to an acene is a very strongly exothermic process (e.g., 3.2 eV for the 1,4 positions of anthracene), the strain energy of the *n*-DEC can be compensated for  $n \geq 12$  resulting in exothermic reactions.
- 6) The barriers for transformations *n*-DDA  $\rightarrow$  *n*-DEC and *n*-DEC  $\rightarrow$  *n*-cylacene + C<sub>2</sub>H<sub>2</sub> depend on the strain energy of the *n*-cylacene.
- 7) The barriers for the reactions from *n*-DDA to *n*-cylacenes are smaller than the CH bond dissociation energies, so that after absorption of an interstellar UV photon by *n*-DDA the interconversion is energetically conceivable.
- 8) As acenes under a critical value of  $n_{cr} \approx 12$ –13 should be efficiently dehydrogenated to *n*-DDA, these are concluded to be converted to *n*-cylacenes after absorption of an interstellar photon of high energy (10–13.6 eV). For larger acenes, the photoprocessing is more complex, but the underlying energetics suggest that *n*-cylacenes could coexist with *n*-acenes.

We feel that acquiring further information on the properties of *n*-cylacenes, especially on their optical spectra, is highly desirable. As laboratory data are currently not within reach, computations of their optical spectra are in our view most important to strengthen the suggestion that *n*-cylacenes could be carriers of some DIBs.

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## Conflict of interest

The authors declare no conflict of interest.

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