PM3 and *ab initio* studies of the C_8H_8 potential energy surface. Thermal isomerism of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes †

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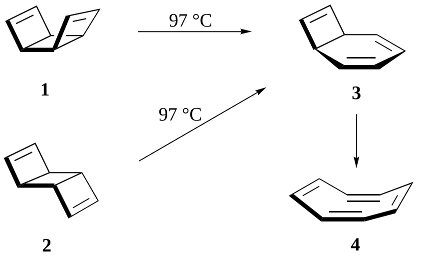
We have identified for the first time symmetry allowed pathways for rearrangement of both the *syn* (1) and *anti* (2) isomers of the cyclobutadiene dimer in the closed shell potential energy surface for the isomerisation to cyclooctatetraene. At the B3LYP/6-31G(d) level of theory, the calculated activation energy for the reaction of 1 is 3.2 kcal mol^{-1} lower than that for 2, in good agreement with the experimental difference of 3.6 kcal mol^{-1}. The possible influence of the σ strain on the synchronicity of the pericyclic reactions of the systems is discussed.

Introduction

The thermal interconversions of C_8H_8 isomers have been the subject of many reports[1] since the synthesis of cyclooctatetraene in 1911.[2] This is certainly due to the fact that cyclooctatetraene (COT) lacks the stabilization of other annulenes and therefore interconverts with its isomers relatively easily. The thermal isomerisation of the *syn* and *anti* isomers of cyclobutadiene[3] dimer (**1** and **2** respectively) to COT (**4**, Scheme 1) was discovered in 1964 by Nenitzescu[4] and has been further studied independently by the Dewar[5] and the Frey[6] groups. Early MINDO/3 calculations[5] by Dewar suggested that the activation energy for the forbidden $_{\pi}2_s + _{\pi}2_s$ cycloelimination to give **4** directly was likely to be very large, and that of the forbidden disrotatory ring opening of **1** to bicyclo[4.2.0]octa-2,4,7-triene (BOT) **3** might be higher than that of the *anti*-isomer **2**, contrary to experiment (a discrimination of 3.6 kcal mol^{-1}, ref. 5, in favour of **1** is found). These results led to the prediction[5] of a crossover to the triplet surface to give triplet **4**. On the other hand, Frey *et al.* discarded a major triplet pathway and suggested a biradical mechanism in which the triplet component of the reaction would depend on the relative rates of intersystem crossing and the rate of conversion of the biradical to BOT.



Scheme 1

Our own interest in this system originates in our search for model systems for studying the relationship between the aromaticity and geometry of pericyclic transition states and the strain in the σ framework. We had previously identified a system[7] where severe σ strain induced gross asynchronicity for the two forming bonds in a $_{\pi}2_s + _{\pi}4_s$ cycloaddition. Shaik, in a series of articles, has recently suggested that the six-fold symmetry of benzene itself is induced by the σ framework rather than by the π aromaticity.[8] This model of geometrical symmetry induced not by aromaticity but by the σ framework has not hithero been evaluated for transition states, and particularly for those such as pericyclic reactions, where both synchronous and asynchronous behaviour can be manifested. We report here new results on the potential energy surface connecting **1** and **2** to **4** which investigate these aspects, and which for the first time establish that formally allowed singlet pathways for the interconversion of **1** and **2** to **4** can exist.

Computational procedure

Initial estimates of the stationary point geometries were obtained by molecular mechanics minimization using the MM2 forcefield in a Tektronix CAChe workstation system. These approximate geometries were then re-optimized at the PM3 level using the MOPAC V6.0 program[9] implemented on CAChe workstations. The transition state structures were located by using the saddle option within MOPAC[10] or the eigenvector following routine (TS) and higher order saddle points were located by minimizing the sum of the squared gradients (NLLSQ). This was followed by calculation of the force constant matrix and normal coordinate analysis to characterize the stationary point, and an intrinsic reaction coordinate calculation along the first normal mode direction to verify the identity of the reactants and products deriving from the transition state. Final values of the gradient norms were <0.01 kcal mol^{-1} Å^{-1} unless indicated. *Ab initio* calculations were performed using PM3 geometries using the GAUSSIAN94 program system,[11] transition states being located by using the Berny algorithm[12] or the synchronous transit-guided quasi-Newton (STQN) methods implemented by Schlegel.[13] Molecular coordinates in the form of Gaussian or Mopac files for located stationary points are integrated into this article in an enhanced on-line form, together with animations of all important imaginary modes showing the form of the eigenvectors.

Results and discussion

The first part of the investigation was to establish if possible pathways existed involving either two concurrent or two consecutive allowed conrotatory 4π-electrocyclic ring openings to give the isomeric chair-cyclooctatetraene structures **8** and **13** respectively (Scheme 2), which could be intermediates on the pathway to **4**. The second part of the investigation requires finding a hithero unstudied pathway from **8** to the tube-COT **4**. An analogous pathway connecting **13** to tube-COT **4** at the MNDO and MINDO/3 levels has been reported previously[14] to involve low energy barriers.

Preliminary calculations established that the bicyclic *trans*-6-ring alkene intermediates **6** and **11** (Tables 1 and 2) were genuine intermediates, but significantly higher in energy than the

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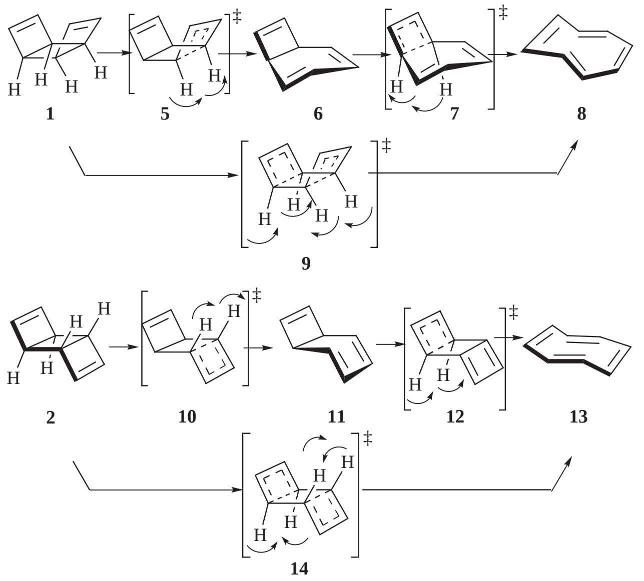
† This article is also available in enhanced multimedia format *via* the World Wide Web: www.rsc.org/ccenhanced.

Table 1 PM3, RHF/6-31G(d) and B3LYP/6-31G(d) energy values for transformation **1**→**4**

	PM3		RHF/6-31G(d)		B3LYP/6-31G(d)
	E − E_1[a]	(ν_1, ν_2)[b]	$E - E_1$[c]	(ν_1, ν_2)[b]	$E - E_1$[e]
1	0		0		0
5	35.79	(−689.6, 211.3)	0.070 768 3 (44.41)	(−598.9, 195.9)	0.051 436 1 (32.28) [−531.4, 191.7]
6	20.01		0.040 986 3 (25.72)		0.028 373 5 (17.80)
7	34.86	(−566.6, 174.8)	0.076 063 9 (47.73)	(−586.6, 225.03)	0.051 861 1 (32.54)
8	−7.73		0.006 558 8 (4.11)		−0.000 318 5 (−0.20)
9	51.48[g]	(−3192.3, −344.7)	0.091 912 6 (57.68)	(−641.8, −382.9)	0.065 348 2 (41.01) [−597.5, −302.6]
17[h]	14.04	(−844.7, 235.2)	0.050 067 8 (31.42)	(−742.0, 213.3)	0.014 820 2 (9.30)
18	−43.21		−0.078 857 6 (−49.48)		−0.754 024 (−47.31)
19	6.74	(−804.1, 204.5)	0.019 181 7 (12.03)	(−701.5, 141.6)	0.012 224 (−7.67)
20	36.06	(−634.5, 243.8)	0.085 571 6 (53.69)	(−590.3, 233.9)	0.050 389 5 (31.62)
21	−25.84		−0.045 363 8 (−28.46)		−0.051 464 8 (−32.29)
22	−17.4	(−1056.4, 201.3)	−0.027 495 7 (−17.25)	(−818.9, 222.7)	−0.050 436 3 (−31.65)

[a] Difference in heat of formation *vs.* **1** (117.50, see footnote *f*) in kcal mol^{-1}. [b] Wave numbers in cm^{-1}. [c] Difference in energy *vs.* **1** (−307.433 105 5) in E_h particle^{-1} (kcal mol^{-1}). [d] Wave numbers in cm^{-1} considering scaling factor of 0.8929. [e] Difference in energy *vs.* **1** (−309.499 396 7) in E_h particle^{-1} (kcal mol^{-1}), $[\nu_1, \nu_2]$ in cm^{-1}. [f] 123.1–123.8 kcal mol^{-1} at the MINDO/3 level (see refs. 20,21). [g] Gradient norm of 0.15 kcal mol^{-1} Å^{-1}. [h] 91.3 kcal mol^{-1} at the MINDO/3 level (see ref. 19).



Scheme 2

cyclooctenes **8** and **13**, because of the significant ring strain induced within the six-membered ring. Concurrent electrocyclic opening of both cyclobutene rings in a synchronous manner *via* **9** or **14** could therefore in principle avoid these high energy intermediates to give **8** or **13** directly. Such a concurrent reaction could in fact also be represented at least formally as a thermally disallowed $_{\sigma}2_{s} + _{\sigma}2_{s}$ cycloelimination. This reaction is thus formally ambiguous in the Woodward–Hoffmann sense, in either representing two concurrent but formally independent four-electron reactions each involving a thermally allowed antarafacial component, or a single four-electron reaction involving no antarafacial components. Formally, one is allowed, the other disallowed by the Woodward–Hoffmann rules, and so it is of some interest to see how the quantitative calculations at the SCF level model the process.

The *trans*-alkene strain in **6** and **11** might be counterbalanced or augmented by aromatic stabilisation/destabilisation for the synchronous geometries **9** or **14**, both formally on the path leading to 8π anti-aromatic products. Schleyer and co-workers have recently reported the 'nucleus independent chemical shift' (NICS)[15] method of estimating aromaticity in both stable systems and in pericyclic transition states, and have tabulated a range of typical values for both aromatic and anti-aromatic systems. We have applied this method to **9** or **14** using probes located respectively at the centres of the middle ring and the external ring (nonweighted mean of the heavy atom coordinates). The stationary point **9** has negative NICS values of −10.2 and −11.9 ppm respectively,[16] clearly in the range designated to be aromatic. On the same scale, benzene has a value of −11.5. The stationary point **14** shows a significantly reduced aromatic character (−6.4 and −6.8 ppm). Therefore both avoidance of strained intermediates and the induced aromaticity geometries would appear to favour the synchronous route for this reaction, but more so for **9** than **14** based on their respective measures of aromaticity.

We next wished to establish if the stationary points **9** and **14** represent more accurately two concurrent electrocyclic ring openings, or single 2 + 2 cycloeliminations. Both are calculated to have two negative force constants at the PM3, and RHF and B3LYP *ab initio* levels (Table 1), indicating they are second-order stationary points. The calculated normal mode corresponding to the most negative force constant **9** can be approximately described as a *bis*-conrotatory ring opening, whilst the motions of the four atoms involved in the cycloaddition/elimination process indicate a significant degree of formally forbidden *supra–supra* character. The less negative force constant shows an anti-symmetric distortion leading to a true, lower energy stepwise transition state **5** (or its mirror image). In contrast, the first equivalent imaginary mode for **14** is subtly different, revealing apparent *bis*-disrotatory ring opening, together with *supra–supra* character for the central formal 2 + 2 elimination. Such a harmonic analysis, corresponding to a quadratic potential surface, is actually misleading. An intrinsic

Table 2 PM3, RHF/6-31G(d) and B3LYP/6-31G(d) energy values for transformation **2**→**4**

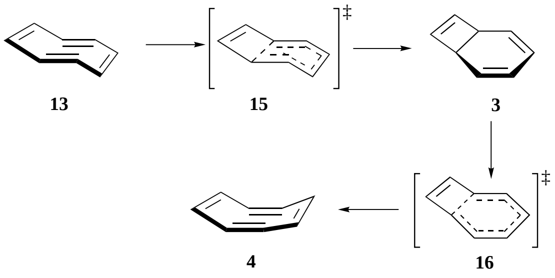
	PM3		RHF/6-31G(d)		B3LYP/6-31G(d)	MNDO[f]	MINDO/3[f]
	$E - E_2$[a]	(ν_1, ν_2)[b]	$E - E_2$[c]	(ν_1, ν_2)[d]	$E - E_1$[e]	ΔH_{298}	ΔH_{298}
2	0		0		0		120.2[i]
10	34.91	(−667.5, 219.7)	0.078 151 3 (49.04)	(−623.7, 210.1)	0.056 552 9 (35.49) [−576.7, 211.2]		
11	21.56		0.053 970 9 (33.87)		0.038 753 (24.32)		
12	38.51	(−582.8, 140.3)	0.098 481 2 (61.80)	(−557.8, 144.6)	*h*		
13	−3.12		0.024 376 1 (15.29)		0.015 758 3 (9.88)		
14	59.52[g]	(−1406.6, −485.0)	0.127 157 (79.79)	(−760.2, −448.3)	0.092 655 6 (58.14) [−682.5, −309.0]		
15	13.5	−931.8, 192.3	0.055 337 4 (34.72)	−871.0, 212.3	0.025 944 2 (16.28)	127.00	128.90
3	−40.04		−0.062 864 3 (−39.45)		−0.058 948 8 (−36.99)	64.30	76.70
16	−10.72	−1040.3, 232.7	−0.007 945 5 (−4.99)	−7383, 134.3	−0.027 885 9 (−17.50)	106.36	99.40
4	−47.41		−0.078 875 9 (−49.49)		−0.074 063 7 (−46.48)	56.44	56.60
23	32.26	−769.9, 256.1	0.079 456 7 (49.86)	−718.5, 252.2	0.047 222 7 (29.63)		
21	−22.32		−0.033 122 4 (−20.78)		−0.041 327 4 (−25.93)		
22	−13.88	−1056.4, 201.3	−0.015 254 3 (−9.57)	−818.9, 222.7	−0.040 298 9 (−25.88)		

[a] Difference in heat of formation *vs.* **2** (113.98) in kcal mol^{-1}. [b] Wave numbers in cm^{-1}. [c] Difference in energy *vs.* **2** (−307.445 346 9) in E_h $particle^{-1}$ (kcal mol^{-1}). [d] Wave numbers in cm^{-1} considering scaling factor of 0.8929. [e] Difference in energy *vs.* **2** (−309.509 534 1) in E_h $particle^{-1}$ (kcal mol^{-1}), $[\nu_1, \nu_2]$ in cm^{-1}. [f] See ref. 14. [g] Gradient norm of 0.43 kcal mol^{-1} Å^{-1}. [h] This structure could not be optimized at this level of theory. [i] See ref. 19.

reaction coordinate (IRC) search using the PM3 potential and starting from **14** reveals that the route to **2** most resembles conrotatory motions of the relevant hydrogens, whilst the route to **13** more closely resembles disrotatory motions. Topologically, two *bis*-disrotatory modes are of course equivalent to two *bis*-conrotatory modes (*supra–supra* = *antara–antara*). This difference between **9** and **14** may well explain the lower degree of aromaticity calculated using the NICS procedure for **14**, and hence its higher relative energy. In one respect therefore **14** is remarkable, exhibiting three formally thermally forbidden pericyclic modes. The second imaginary mode in **14** is again an anti-symmetric distortion leading to lower energy **10** (Table 1). Both **5** and **10** show only a single negative force constant, with the corresponding eigenvectors corresponding to conrotatory ring openings.

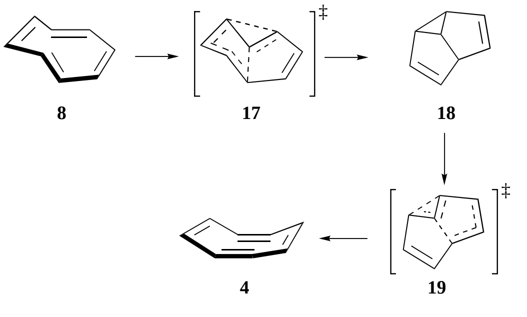
The B3LYP level energy difference **9** − **5** of 8.7 kcal mol^{-1} was much smaller than **14** − **10** (22.6 kcal mol^{-1}), in accord with the greater aromatic stabilisation of **9** compared with **14**. This clearly indicates that in this system at least, avoidance of ring strain in the product is not sufficient to induce synchronicity in the transition state, but it does raise the intriguing possibility that appropriate substituents that might stabilise the extended aromaticity could lower the energy of the synchronous geometry to the point that it becomes a genuine transition state.

We next have to establish that **5** and **10** represent the rate limiting transition states in the surface, and that closed shell pathways to **4** can be found. First, we note that both **6** and **11** can convert to **8** and **13** respectively *via* transition states **7** and **12**. These both exhibit the conrotatory imaginary modes expected from thermal opening of a cyclobutene rather than the disrotatory mode expected for opening of a cyclohexadiene. In this, both **7** and **12** represent examples of a formally disallowed 6π-thermal process, but in fact avoid this by having one of the spectator alkene bonds essentially orthogonal to the remaining π system. The existence of chair-COT **13** has been the object of previous speculation.[14] The studies reported a tendency of isomerisation to the more stable tube-COT **4** according to the reaction in Scheme 3.



Scheme 3

Table 2 shows the comparison between the previous MNDO and MINDO/3[14] results and those obtained at the PM3, RHF/6-31G(d) and B3LYP/6-31G(d) levels. No transition state for the analogous transformation (chair-COT **8** to tube-COT **4**) could be located, and the isomerisation of **8** to **13** by rotating along two single bonds was of high energy at the PM3 level (166.91 kcal mol^{-1}). However, a transition state which connects chair-COT **8** and semibulvalene **18** could be found (Scheme 4).



Scheme 4

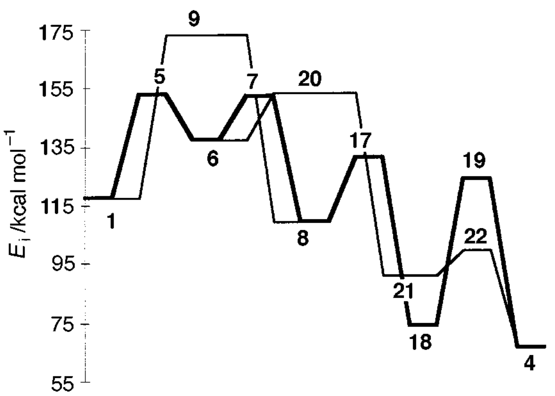


Fig. 1 PM3 potential energy surface for transformation **1**→**4**. Energy in kcal mol^{-1}.

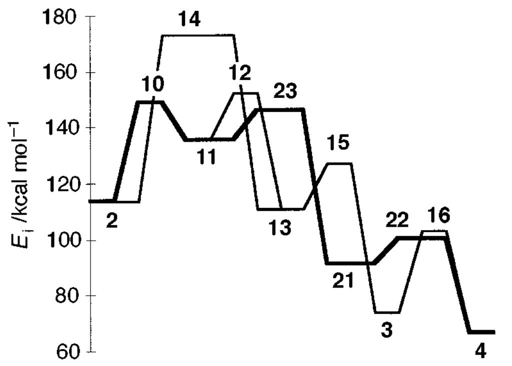
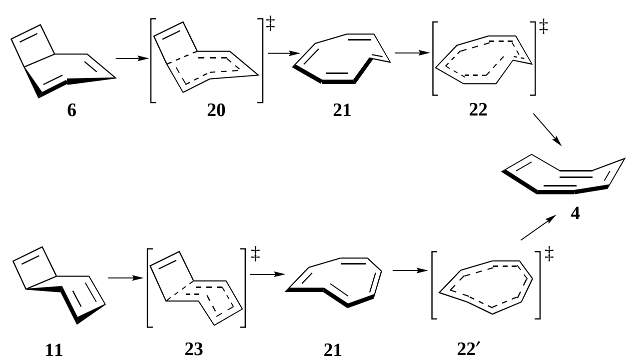


Fig. 2 PM3 potential energy surface for transformation **2**→**4**. Energy in kcal mol^{-1}.

Since the interconnection between semibulvalene **18** and tube-COT **4** has been described[17] this seemed to be a suitable pathway for the isomerisation of **8** to **4**. However, both PM3 and *ab initio* calculations predict a large barrier energy for the transformation **18**→**4** (Table 1).

Next, we considered the possibility of an allowed 6π-disrotatory ring opening of the intermediates **6** and **11** to give *via* transition states **20** and **23** the *trans*-cyclooctatetraene **21**. The latter compound is known to be obtained at room temperature[18] but could undergo further isomerisation to tube-COT **4** at the conditions under discussion (Scheme 5). The ring opening would be formally identical to the valence isomerisation of BOT→COT. The energies of **20**, **22** and **23** are lower than the initial transition state **5** and **10** (Tables 1 and 2), establishing the latter as the rate-limiting species.



Scheme 5

Compound **11** could undergo a formal conrotatory 4π-ring opening (Scheme 2) to **13** *via* transition state **12** or a formal 6π-ring opening (Scheme 5) to **21** *via* transition state **23**. The imaginary mode for **23** is unusual in resembling neither dis- nor con-rotation, one hydrogen rotating and the other not. Perhaps such a mode avoids the contradiction that either dis- or con-

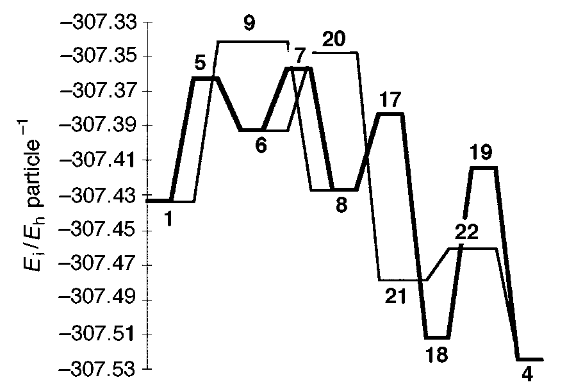


Fig. 3 RHF/6-31G(d) potential energy surface for transformation **1**→**4**. Energy in E_h particle^{-1}.

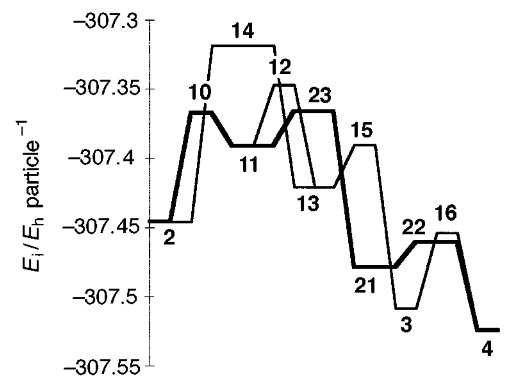


Fig. 4 RHF/6-31G(d) potential energy surface for transformation **2**→**4**. Energy in E_h particle^{-1}.

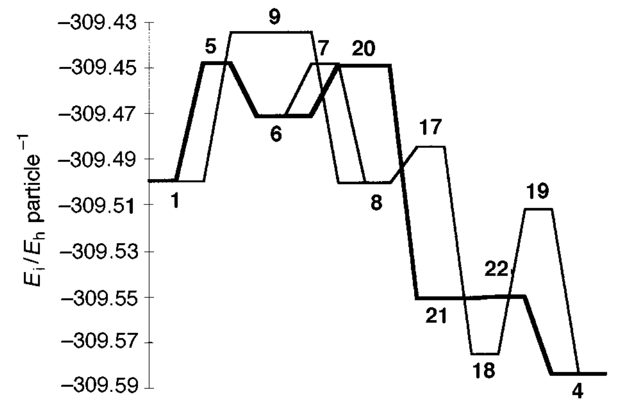


Fig. 5 B3LYP/6-31G(d) potential energy surface for transformation **1**→**4**. Energy in E_h particle^{-1}.

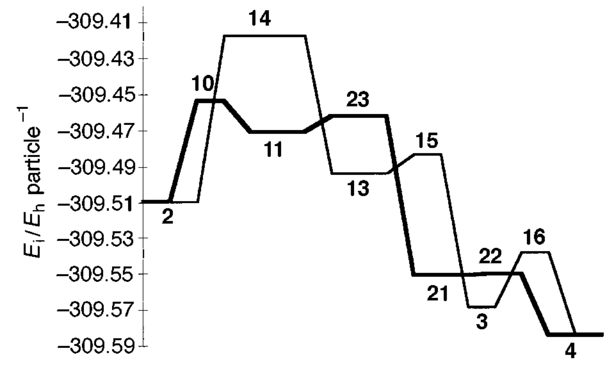


Fig. 6 B3LYP/6-31G(d) potential energy surface for transformation **2**→**4**. Energy in E_h particle^{-1}.

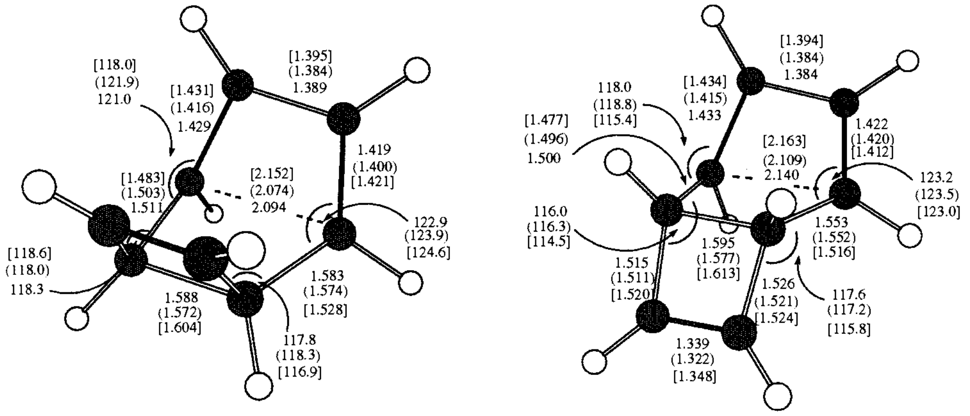


Fig. 7 B3LYP/6-31G(d) [RFH/6-31G(d)] [PM3] optimised geometries (distances in Å and angles in degrees) for compounds **5** and **10**

rotatory openings would violate the Woodward–Hoffmann rules. The route *via* **23** is slightly favoured energetically over **12**, and the intermediate **21** could in turn readily evolve to tube-COT **4** through π-bond shifting. This latter seems to be the pathway of lowest overall energy (Figs. 2, 4 and 6). The bond shifting transition state for the transformation **21**→**4** would not be planar and therefore of lower symmetry than the reported transition state for the bond shifting in tube-COT.[19] For compound **6**, at PM3 and RHF/6-31G(d) levels, a 4π-ring opening to **8** (Scheme 2) would have a lower barrier energy than the 6π-ring opening to **21** (Scheme 5) but the pathway through **8** would imply the formation of **18** and the high energetic transformation **18**→**4** (Figs. 1 and 3). The DFT [B3LYP/6-31G(d)] results are in favor of the 6π-ring opening **6**→**21** (Scheme 5, Fig. 5) and in this case all the subsequent energy barriers would be accessible.

On the basis that **5** and **10** represent the genuine transition for the overall reactions, the activation energies obtained on this basis at the DFT level ($\Delta H^\ddagger$ 32.3 and 35.5 kcal mol^{-1} for **1**→**5**→**4** and **2**→**10**→**4** respectively) are in good agreement with those obtained experimentally ($E_a = 28.8$–30.5 and 32.4–32.6 kcal mol^{-1} respectively[5,6]). Fig. 7 shows the geometry of both transition state structures (**5** and **10**) that determine the activation energies. Finally we note that the activation energy for reaction of **1** is 3.2 kcal mol^{-1} lower than for **2**, in good agreement with the experimental measurement of 3.6 kcal mol^{-1}, ref. 5.

Conclusions

According to DFT *ab initio* calculations, the thermal isomerisation of the *syn*- and *anti*-dimers of cyclobutadiene **1** and **2** to cyclooctatetraene **4** can take place without the involvement of triplet states, contrary to a previous report. The newly proposed pathway consists of a symmetry-allowed 4π-conrotatory ring opening giving high strained 2-cis,4-*trans*,6-*cis*-bicyclo[4.2.0]-octa-2,4,6-trienes **6** and **11** as the rate determining step. The pathway involving synchronous breaking of two σ-bonds is not promoted by avoidance of these strained intermediates, but there is some evidence that the relative aromaticity of the synchronous stationary point **9** does in part offset the ring strain in **6**. Intermediates **6** and **11** could readily undergo a further allowed 6π-ring opening to 1-*cis*,3-*cis*,5-*cis*,7-*trans*-cyclooctatetraene **21**, and the latter could isomerise through a π-bond shifting to the more stable 1-*cis*,3-*cis*,5-*cis*,7-*cis*-cyclooctatetraene **4**.

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