Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 6771

www.rsc.org/obc

PAPER

Thermal reaction of [3,4]-benzo-8-substituted-3*Z*,5*Z*,7*E*-octatetraenes and quantum-chemical study of the (8π,6π)-electrocyclisation†

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Received 23rd May 2011, Accepted 30th June 2011
DOI: 10.1039/c1ob05802a

The first example of thermal (8π,6π)-electrocyclisation of 1,3,5,7-octatetraene with one double bond embedded in an aromatic moiety is described. By this process, [3,4]-benzo-8-substituted octatetraene derivatives, the *cis*,*trans*-1-(*o*-vinylphenyl)-4-(R = Me, Ph, 2-furyl)buta-1,3-dienes were transformed to a new *endo*-7-(R = Me, Ph, 2-furyl) and *exo*-7-(R = Me)-2,3-benzobicyclo[4.2.0]octa-2,4-dienes. Mechanism of reaction was also studied by DFT quantum-chemical calculations. The M06/6-311+G(d,p)//M06/6-31+G(d,p) calculations indicate that formation of the single *endo*-isomer in the case of phenyl and 2-furyl substituents is determined by higher activation barriers for *exo*-6π-electrocyclisation than for 8π-cycloreversion.

Introduction

Electrocyclic reactions present an important synthetic entry to complex polycyclic structures.[1] In this class of pericyclic reactions conjugated polyene interconverts with an unsaturated cyclic compound containing one carbon-carbon double bond less than the starting polyene. These reactions can be promoted thermally or photochemically and take place with a very high degree of stereoselectivity, which could be interpreted on the basis of the Woodward–Hoffmann selection rules.[2] Some of the reactions within this class of reactions are of biosynthetic importance.[3] For instance, it is assumed that bicyclo[4.2.0]octadiene skeleton, commonly found in natural compounds, arises biosynthetically from 8π,6π electrocyclization cascades.[4] Such cascades have been proposed by Black in the biosynthesis of the endiandric acids,[5] as well as by Baldwin and Trauner in the synthesis of immunosuppressants SNF4435 C D^{-1},[6–8] which was later verified by total synthesis by Nicolaou.[9] Electrocyclase enzymes are even proposed by Rickards to support six π-electron electrocyclic reactions *in vivo*.[10] Thermolysis of several cyclooctatraene derivatives following the 8π,6π electrocyclization reaction mechanism has been reported in the literature, and in all cases configuration around the double bonds was found to be crucial for reactivity.[11,12] Typical examples are provided by compounds **1**[13] and **2**[6,7] (Chart 1). In molecules **1** and **2** in which substituents are attached at the *termini* of tetraene moiety 8π,6π-electrocyclization readily takes place. In contrast, the 6π-electrocyclization of tetraene **3** does not follow an initial 8π-electrocyclisation step.[14] The 6π-electrocyclization also does not take place in octatetraene derivatives with the C=C bonds embedded into dihydropyran[15] or cyclohexene[16] rings.

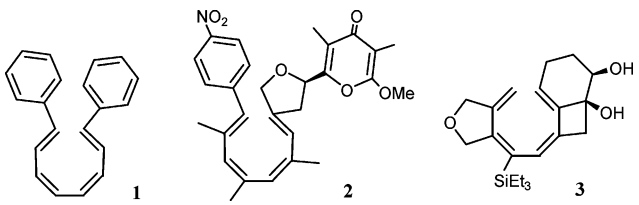
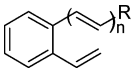


Chart 1 Literature examples of octatetraene systems **1–3** undergoing 8π,6π electrocyclisations.[13–16]

As a part of our longstanding interest in intramolecular photocycloaddition reactions of heteroaryl substituted hexatrienes **4** (*n* = 1, Chart 2) with one double bond incorporated into the benzene ring[17] we recently reported synthesis and photocycloadditions of novel *o*-butadienylstyrenes **5** (*n* = 2).[18] In continuation of this work we here present results of experimental and computational study[19] of thermal reactions of the latter compounds. The aim of this study was twofold: 1) to investigate 8π,6π-electrocyclizations of novel *o*-butadienylstyrenes, where conjugated tetraene π-system is at the



4 n = 1
5 n = 2

R = Me, Ph, Furyl, etc.

Chart 2 Octatetraene *o*-butadienylstyrene systems.

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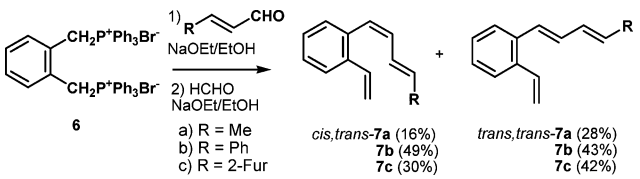
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C spectra of all new compounds and Cartesian coordinates for optimized structures. See DOI: 10.1039/c1ob05802a

same time part of an aromatic moiety, and 2) to gain insight into the reaction mechanism and experimentally observed selectivities.

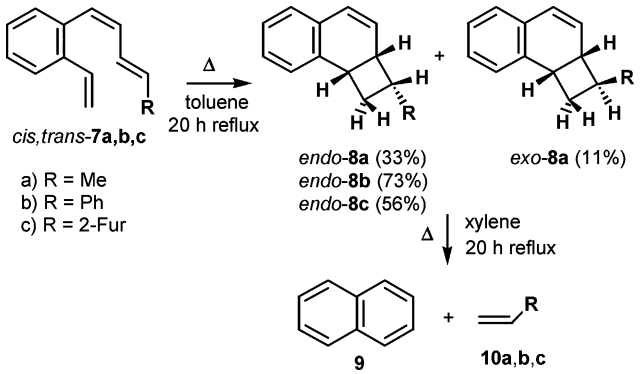
Results and discussion

The compounds were prepared employing one-pot synthetic approach based on double Wittig reaction, starting from an aromatic diphosphonium salt **6** and two different aldehydes (Scheme 1) developed earlier in one of our groups.[20] Using commercially available crotonaldehyde (R = Me), cinnamaldehyde (R = Ph) or furylacrylaldehyde (R = 2-furyl) in their *trans*-configurations, respectively, and proper addition strategy of these aldehydes, formaldehyde and base the *cis*,*trans*-**7** and *trans*,*trans*-**7** isomers were obtained in good yields.



Scheme 1 Synthesis of benzooctatetraenes **7a–c**.

Reactivity of all three *cis*,*trans*-benzooctatetraenes **7a–c** was explored under thermal conditions (Scheme 2). In accordance with available literature data on thermal 8π,6π-electrocyclizations, our results showed that incorporation of octatetraene π-system in the aromatic ring requires significantly higher temperatures for cyclisation to take place (toluene reflux) than octatetraenes substituted at termini (such as **1** and **2**). On reflux **7a** in toluene (111 °C, 20 h), a mixture of two isomeric products, *endo*- and *exo*-7-methyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene **8a** in 3 : 1 ratio in 44% overall yield was obtained (Fig. 1). The stereochemistry of the two isomers was deduced from 2D COSY, NOESY and HSQC NMR experiments, the most indicative being NOESY correlations and aromatic shielding of the methyl group of *endo*-**8a** in the ^{1}H NMR spectrum. On the contrary, replacement of the terminal



Scheme 2 Thermal reaction of benzooctatetraenes **7a**,**b**,**c**.

methyl group by a furyl or phenyl moiety led to a stereospecific reaction. In the case of *cis*,*trans*-**7b** (or **7c**), only one stereomeric product *endo*-**8b** (or **8c**)[5] was obtained (toluene, 20 h, in 73 and 56% yield, respectively). On reflux in benzene (80 °C, 20 h) phenyl derivative **7b** was converted to benzobicyclo[4.2.0]octa-2,4-diene **8b** in only 20% yield. The highest yield obtained was 73%, as the consequence of prolongued heating of thermally unstable octatetraenes, which at higher temperatures also undergo thermolysis to intractable products. Refluxing of *cis*,*trans*-**7b** in xylene (144 °C, 20 h) resulted in complete disappearance of the reactant, with only traces of **8b** present, presumably due to ring cleavage to naphthalene **9** and the corresponding vinyl derivatives **10a–c** (Scheme 2). This was corroborated by analysis of ^{1}H NMR spectra of the thermolysis products of **7b** and **7c** in xylene, which showed only presence of naphthalene, styrene **10b** and 2-vinylfuran **10c**. Furthermore, GC-MS analysis of a mixture of *cis*,*trans*- and *trans*,*trans*-compounds **7** showed presence of only *trans*,*trans*-**7** isomer, along with a new signal (M^+ 128) which is associated to naphthalene **9**.

The possibility of formation of products **8a–c** *via* photochemical pathways was also tested. Similarly to the previously published results for **7b** and **7c** benzooctatetraene derivatives[18] the methyl

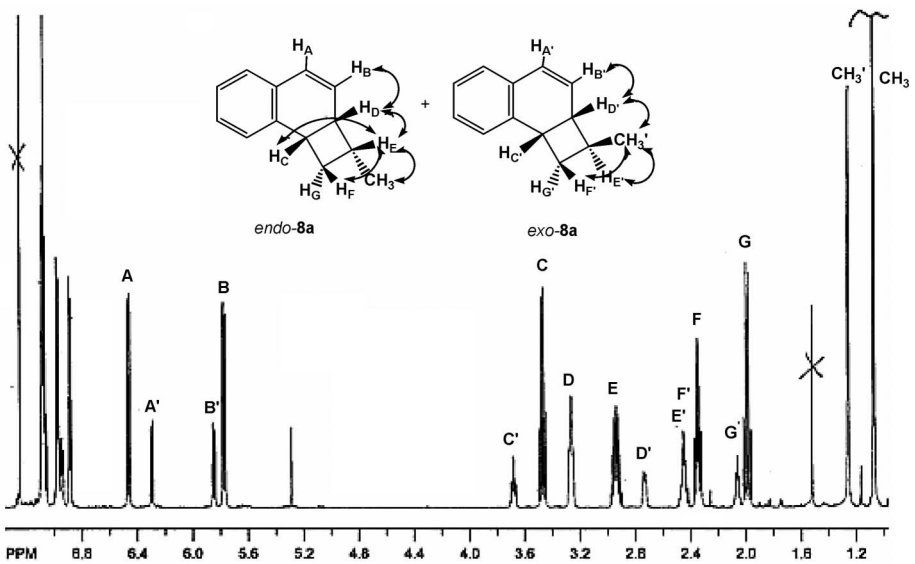
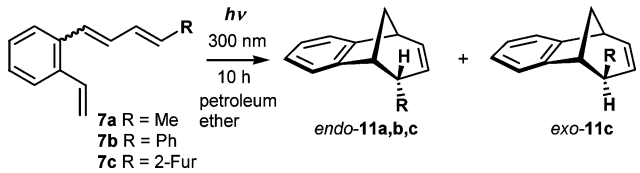


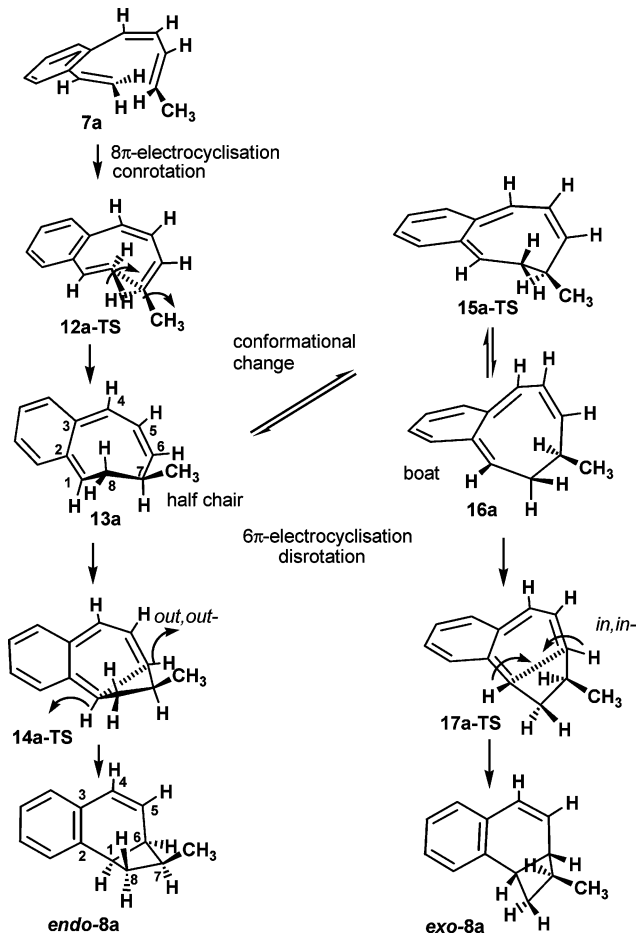
Fig. 1 NMR spectrum of reaction mixture of **8a** in toluene and selected NOESY correlations.

derivative **7a**, was found to undergo intramolecular photocycloaddition affording *endo*-7-methyl-2,3-benzobicyclo[3.2.1]octa-2,5-diene **11a** as the main product, although in a significantly lower yield (26%) than previously obtained for *endo*-7-phenyl/furyl-2,3-benzobicyclo[3.2.1]octa-2,5-dienes **11b** and **11c** (90% and 57% yield, respectively, Scheme 3). Most importantly for the current thermal study is that *exo*/*endo* products **8a–c** were not detected spectroscopically in the photochemical [2 + 2] cycloaddition pathway.



Scheme 3 Photochemical reaction of benzooctatetraenes **7a–c**.

The proposed reaction mechanism for transformation of **7a–c** to *endo*/*exo*-**8a–c** involves an 8π,6π-electrocyclization cascade,[21] as depicted in Scheme 4 using **7a** as an example. According to the Woodward–Hoffmann selection rules,[22] in the first step (8π-electrocyclization) conrotatory ring closure *via* transition state **12a-TS** takes place.[23] At this point, final stereochemistry at C7 and C8 is defined, leading to an intermediate pentaene **13a**. Aromaticity of benzene moiety is restored in the second reaction step, (disrotatory 6π-electrocyclization), *via* **14a-TS**, which defines configurations at C1 and C6 atoms of *endo*-**8a**. To obtain *exo*-**8a** product, conformational interconversion (ring flipping of the CH_2 group) of the intermediate **13a** (half chair conformation) takes place *via* transition state **15a-TS** to boat conformer **16a**. In analogy to the intermediate **13a**, disrotatory 6π-electrocyclization of intermediate **16a** involving transition state **17a-TS**, leads to the product *exo*-**8a**.



Scheme 4 Mechanism proposed for thermal electrocyclisation of **7a**.

Computational study

In order to gain deeper insight into factors determining experimentally observed stereospecificity of thermal electrocyclization of the studied compounds, we carried out a quantum-chemical study of the reaction mechanism for all three compounds. For this purpose, the M06/6-311+G(d,p)//M06/6-31+G(d,p) computational method was used. The M06 is a novel hybrid *meta* functional with good accuracy for applications involving main group thermochemistry, kinetics and barrier heights.[24] The M06 calculations are expected to provide a more fair comparison of the energetics, since recent calculations have established that M06 leads to activation energies a few kcal mol^{-1} more accurate than B3LYP for pericyclic reactions.[25,26] Optimized structures of reactants, intermediates and transition states are visualized in Fig. 2, while Fig. 3 and 4 depict reaction energy diagrams. So far, 6π- and 8π-electrocyclisations of substituted octatetraenes were scarcely studied computationally, employing PM3,[27] MINDO/3,[28] 3-21G,[29] 6-31G(d),[30] B3LYP/6-31G(d),[31] and B3PW91/6-31G(d,p)[32] methods. This work, to the best of our knowledge, is the first computational study of domino 8π,6π-electrocyclizations.

Geometries. Firstly we focussed on the geometries of the stationary points found in calculations of rearrangement of the methyl derivatives **7a–17a**. The M06/6-31G+(d,p) calculated geometry of **12a-TS** qualitatively resembles B3LYP3/6-31G(d,p) optimised TS structure for conrotatory 8π-electrocyclisation of a series of octa-1,3,5,7-tetraenes reported previously by Cossio.[31] The most characteristic structural features of **12a-TS** encompass the length of new forming C7 · · · C8 bond (2.096 Å, for numbering see Scheme 4) and its helical conformation which allows almost perfect eclipsing between the terminal C1 and C8 atoms. The alternation of double bonds present in the starting tetraene is partially preserved in **12a-TS** (Fig. 2). In addition, geometry constraint present in the case of 6π-electrocyclisation is reflected in elongation of the new forming C1 · · · C6 bond in **14a-TS** (2.333 Å) and **17a-TS** (2.346 Å), as compared with **12a-TS** (2.096 Å).

The lengths of the new forming C7 · · · C8 bonds in phenyl and furyl substituted transition states **12b-TS** and **12c-TS** are significantly shorter than in **12a-TS** (2.064 Å and 2.062 Å, respectively), due to the change of electronic nature and conjugation of substituents attached to the C7 carbon atom. On the other hand, the differences in lengths of the new forming C1 · · · C6 bonds for phenyl and furyl substituted transition states relative to **14a-TS** and **17a-TS** are less pronounced (2.329, 2.346, 2.354, and 2.356 Å, for **14b-TS** (**14c-TS**) and **17b-TS** (**17b-TS**), respectively). The structural similarity of the transition states for 6π-electrocyclisation could be explained by the fact that substituent is further away from the reacting carbon atom.

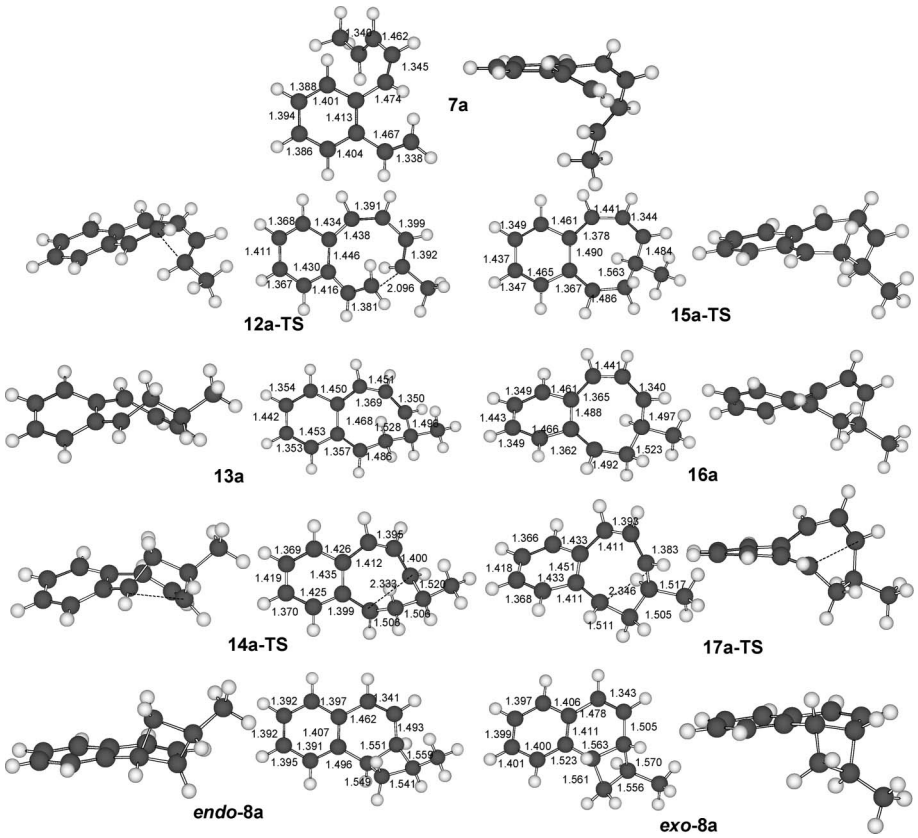


Fig. 2 Reactants, intermediates and transition state structures (top and side-views) for electrocyclization of **7a** optimized by M06/6-31+G(d,p) method (selected bond distances are given in Å).

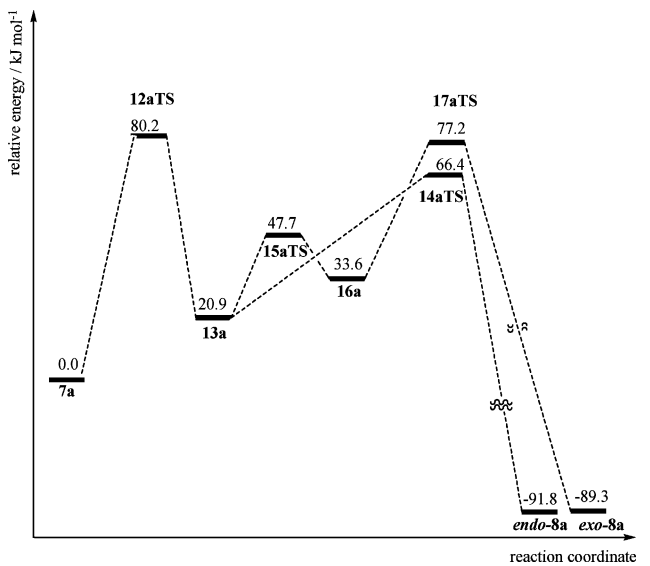


Fig. 3 Reaction energy profile for thermal electrocyclization of **7a** calculated at the M06/6-311+G(d,p)//M06/6-31+G(d,p)+ZPVE level of theory. Relative energies are given in kJ mol^{-1} and zero point energy corrections are included.

Energetics. Relative energies for all species postulated to be involved in the mechanism of thermal electrocyclisation of **7a–c** calculated by M06/6-311+G(d,p)//M06/6-31+G(d,p)+ZPVE method are collected in Table 1 and depicted in Fig. 3 and 4.[33] In the

Table 1 Relative energies (kJ mol^{-1}) calculated at the M06/6-311+G(d,p)//M06/6-31+G(d,p)+ZPVE level of theory of methyl, phenyl and furyl derivatives, with zero point energy corrections included

Molecule	a (R = methyl)	b (R = phenyl)	c (R = furyl)
7(a-c)	0.0	0.0	0.0
12(a-c)-TS	80.2	84.7	94.0
13(a-c)	20.9	36.6	46.0
14(a-c)-TS	47.7	66.7	75.3
15(a-c)-TS	33.6	52.5	59.6
16(a-c)	66.4	88.0	96.4
17(a-c)-TS	77.2	97.3	103.6
***endo*-8(a-c)**	–91.8	–74.5	–68.8
***exo*-8(a-c)**	–89.3	–72.6	–67.5

M06 calculations, the barriers for conformational interconversions are lower than the barriers for product formation. Under such circumstances, as dictated by the Curtin-Hammett principle, the energies of the conformations and the low barriers for their interconversion are irrelevant, and the ratio of the products is decided by the energies of the rate-limiting transition states leading to the products. The assumption that the conformational energies or barriers are a deciding factor in the observed selectivities is not in accord with the obtained energies in combination with basic chemical principles.

We shall first discuss thermal electrocyclisation of **7a** in some detail. Energy barrier necessary for formation of intermediate **13a** *via* transition state **12a-TS** is 80.2 kJ mol^{-1}. This barrier is significantly higher than the value calculated for the parent

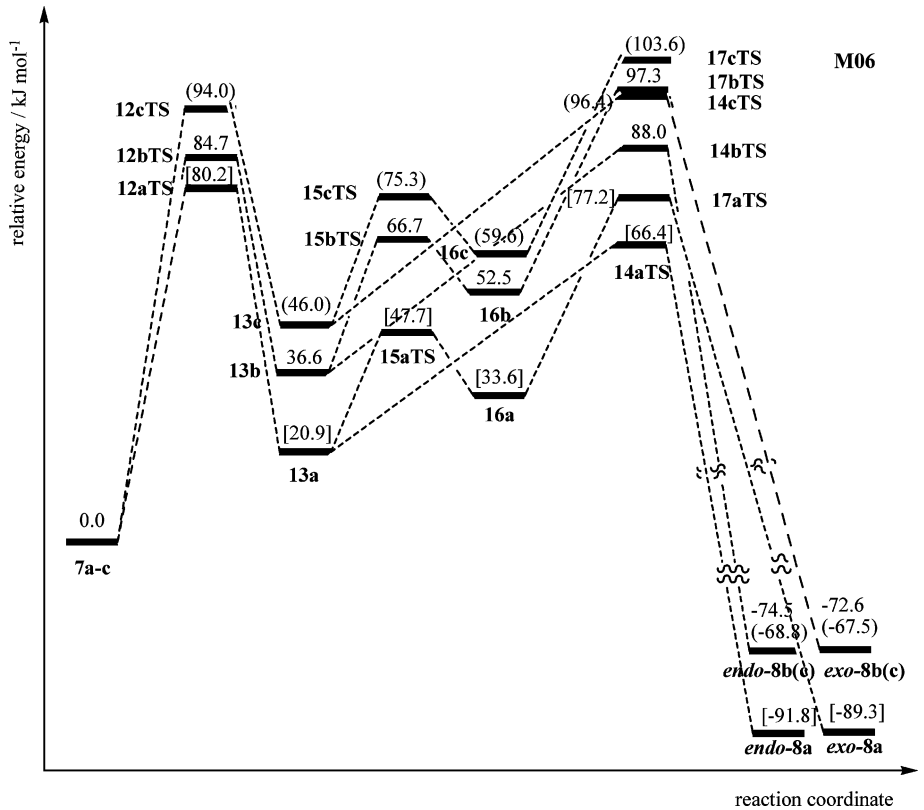


Fig. 4 Reaction energy profile for thermal electrocyclization of **7a–c** calculated at the M06/6-311+G(d,p)//M06/6-31+G(d,p)+ZPVE level of theory (results for **7a** are given in square brackets and for **7c** in angle brackets). Relative energies are given in kJ mol^{-1} and zero point energy corrections are included.

unsubstituted octatetraene at the same level of theory (13.0 kJ mol^{-1}), or by Houk (MP2/6-31G(d), 33.5 kJ mol^{-1}).[30] The consequent conformational change **13a**→**16a** *via* transition state **15a-TS** requires 26.8 kJ mol^{-1} (Fig. 3, Table 1). This value implies facile **13a**↔**16a** interconversion. In other words, it is possible for the intermediate **13a** to react in two ways. In a first, energetically more accessible way, it is necessary to bring 45.5 kJ mol^{-1} to proceed directly to the *endo*-**8a** product *via* transition state **14a-TS** (Fig. 3, Table 1). The reaction which would lead back to the reactant is energetically less favorable due to the larger barrier of 59.3 kJ mol^{-1}. Since the conformational change **13a**→**16a** is feasible, intermediate **13a** could alter its conformation and form the less stable isomer **16a**. Subsequently the *exo*-**8a** product is readily obtained *via* transition state **17a-TS**, since the energy barrier for this reaction is lower than the barrier for the back reaction which would lead to reactant **7a** (77.2 *vs.* 80.2 kJ mol^{-1}, respectively). The energy profile indicates that activation energies for 6π-electrocyclisation leading to the formation of either *endo*- or *exo*-products are lower than for their interconversion back to reactant **7a** *via* **12a-TS**, thus enabling formation of both *endo* and *exo* products, as experimentally observed. Considering that the reaction path which results in the *exo* product includes energetically costly conformational change and higher activation energy for the final 6π-electrocyclisation, it is less favorable. These results are in good accord with the experimentally observed product ratio of 3 : 1, with the *endo*-**8a** product more abundant.

In phenyl and furyl substituted octatetraenes **7b** and **7c**, the reaction outcome is quite different and only *endo* products were formed. It was found that the energy barrier for the formation of intermediate **16b** *via* conformational change **13b**→**16b** in phenyl derivative is 66.7 kJ/mol. This value is by 18.0 kJ mol^{-1} lower than the activation barrier for the formation of intermediate **13b** from **7b** (Fig. 4, Table 1). Similarly, in the case of furyl substituted octatetraene **7c** energy for the formation of **16c** *via* conformational change **13c**→**16c** equals 75.3 kJ mol^{-1}, which is by 18.7 kJ mol^{-1} lower than activation barrier for the formation of intermediate **13c** from **7c**. These results suggest that the conformational changes **13b(c)**→**16b(c)** are energetically feasible. However, there is a significant difference from the reaction energy profile of tetraene **7a** (Fig. 3), which explains experimentally observed selectivities. Activation barriers for 6π-electrocyclisation leading to *endo*/*exo*-**8b(c)** products (*via* transition states **14b(c)-TS** and **17(c)-TS**) are notably equal or even higher than for 8π-electrocyclisation (transition states **12b(c)-TS**). In the case of phenyl derivative **7b**, activation barriers are 84.7, 88.0 and 97.3 kJ mol^{-1} (for **12b-TS**, **14b-TS** and **17b-TS**, respectively), while for furyl derivative **7c** activation barriers are 94.0, 96.4 and 103.6 kJ mol^{-1} (for **12c-TS**, **14c-TS** and **17c-TS**, respectively). On the other hand, in the case of methyl substituted tetraene **7a**, activation barriers are 80.2, 66.4 and 77.2 kJ mol^{-1} (for **12a-TS**, **14a-TS** and **17a-TS**, respectively). These differences indicate that reaction **13b(c)**→*endo*-**8b(c)** which would lead to the *endo* product is energetically more accessible and only the *endo* product is formed for phenyl and furyl derivatives.

Table 2 Gibbs free energy of solvation (ΔG_{solv}) calculated by CPCM/HF/6-31G(d)//M06/6-31+G(d,p) method (kJ mol^{-1})

Molecule	a (R = methyl)	b (R = phenyl)	c (R = furyl)
7(a-c)	4.1	5.0	2.5
12(a-c)-TS	−5.4	−2.7	−4.9
13(a-c)	−6.4	−3.6	−5.3
14(a-c)-TS	−6.9	−4.5	−5.0
15(a-c)-TS	−6.3	−4.3	−4.9
16(a-c)	−5.7	−3.8	−5.0
17(a-c)-TS	−6.0	−4.1	−4.4
***endo*-8(a-c)**	−4.2	−2.6	−4.1
***exo*-8(a-c)**	−3.3	−3.3	−4.4

Higher energy than required for 8π-electrocyclisation (*via* **12b(c)-TS**) would ultimately favor energetically lower electrocyclic ring opening reaction **13b(c)→7b(c)** and would lead back to the reactants.[34]

The presented computational results for thermal 8π,6π-electrocyclizations are in good accordance with experimental results which indicate that incorporation of octatetraene π-system in aromatic ring requires significantly higher temperatures for 8π-electrocyclization to take place than for octatetraene systems such as **1** and **2** (toluene reflux, Scheme 2).

We also evaluated the effect of solvent on the course of the studied reactions using CPCM/HF/6-31G(d) method (Table 2). Single point CPCM/HF/6-31G(d) energies were calculated for the M06/6-31+G(d,p) optimized structures in the gas phase. For this purpose calculations were carried out with toluene as a solvent, which was also used experimentally. The results of the calculation of Gibbs free energy of solvation (ΔG_{solv}) indicate that the *endo*-selectivity is retained in the calculations carried out in toluene as expected for an intramolecular reaction in nonpolar solvent. Analysis of the data presented in the Table 2 reveals that reactants are slightly destabilized upon solvation (2.5–5.0 kJ mol^{-1}), whereas intermediates and products become stabilized upon solvation (2.6–6.9 kJ mol^{-1}). However, these subtle energy differences are not large enough to induce the reversal of the *endo*-selectivity. This is expected since the interaction between nonpolar solutes and nonpolar solvent, such as toluene, is relatively weak.

Conclusions

Cis,*trans*-1-(*o*-vinylphenyl)-4-(R = Me, Ph, 2-furyl)buta-1,3-dienes, with one double bond embedded in aromatic ring undergo thermal 8π,6π-electrocyclisation giving *endo*-7-(R = Me, Ph, 2-furyl) and *exo*-7-(R = Me)-2,3-benzobicyclo[4.2.0]octa-2,4-dienes. Quantum-chemical calculations at the M06/6-311+G(d,p)//M06/6-31+G(d,p) level of theory indicate that formation of the single *endo*-product in the case of phenyl and 2-furyl substituents is determined by the high activation barrier for formation of *exo*-products in 6π-electrocyclisation. These energy barriers are higher than activation energy for 6π-electrocyclisation leading to the *endo*-products, or activation barrier for electrocyclic ring opening to the starting **7b(c)**. In the case of methyl derivative **7a**, energy barriers for 6π-electrocyclisation leading to either *endo*- or *exo*-product are significantly lower, therefore enabling formation of both isomeric products. The *endo*-selectivity obtained in gas-phase calculations is retained in **7b(c)**, when solvent effects were evaluated by means of Gibbs free energy of solvation (ΔG_{solv}).

Experimental details

The NMR spectra were recorded in $CDCl_3$ solutions containing tetramethylsilane as internal standard on Bruker AMX 300 or 600 MHz spectrometers. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. The mass spectra were recorded on a GC-MS instrument Varian Saturn 2200 (capillary column FactorFour VF-5 ms, GC temperature program: delay 3 min, injector temperature 350 °C, heating from 110–300 °C within 6 min, then 300 °C isotherma for 7 min). Microanalyses were performed on a PerkinElmer 2400 Series II CHNS/O Analyzer. UV spectra were recorded on Varian Cary 50 UV/VIS spectrophotometer. Chromatographic separations were performed on silica gel columns (Kemika, Merck, Across 0,063–0,2 nm) and thin layer plates (silica gel 0.2 mm, Kieselgel 60 F_{254}, Merck). All preparative irradiation experiments were carried out in 10^{-2}–10^{-3} molar solutions in a Quartz tube and in a Rayonet reactor equipped with RPR 3000 Å lamps. All solvents were distilled prior the use. Crotonaldehyde and paraformaldehyde were purchased from Aldrich, while known procedures were used to prepare substrates **7b** and **7c**[18] and diphosphonium salt of α,α'-*o*-xylylenedibromide.

cis,*trans*-1-(*o*-Vinylphenyl)penta-1,3-diene (*cis*,*trans*-7a) and *trans*,*trans*-1-(*o*-vinylphenyl)penta-1,3-diene (*trans*,*trans*-7a)

A three-necked round bottomed flask was charged with absolute ethanol (250 mL). Diphosphonium salt (7.88 g, 0.01 mol) was added under nitrogen atmosphere (which is partially dissolved), followed by *trans*-crotonaldehyde (0.77 g, 0.011 mol). To this mixture, solution of sodium ethoxide (prepared from sodium (0.269 g, 0.012 mol) and ethanol (10 mL)) was added dropwise. The formation of ylide is indicated by the formation of a yellow color, which disappears on further reaction. After one hour, under a stream of dry nitrogen, gaseous formaldehyde (obtained by decomposition of paraformaldehyde taken in excess, 2 g, 0.066 mol) and a solution of sodium ethoxide (prepared from sodium (0.23 g, 0.01 mol) in ethanol (10 mL) were simultaneously added and stirred at room temperature for one hour. Ethanol was removed under reduced pressure, water was added and product was extracted with benzene (3 × 20 mL). Organic extracts were collected, dried over $MgSO_4$ and solvent removed in vacuo. The product was extracted from the residue with petroleum ether, which was subsequently evaporated. The residue was dissolved in chloroform and purified by column chromatography (silica gel, petroleum ether) to obtain purified mixture of isomers in 44,4% yield. Separation of isomers was achieved by additional column chromatography (silica gel, petroleum ether), in order of elution *cis*,*trans*-**7a**, followed by *trans*,*trans*-**7a**.

cis,*trans*-1-(*o*-Vinylphenyl)penta-1,3-diene (*cis*,*trans*-7a)

Colorless oil, (yield 16%). UV (EtOH) λ_{max}/nm (log ε /dm^3 mol^{-1} cm^{-1}): 271 (4.05, sh), 246 (4.16): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.53 (m, 1H, H_{ar}), 7.25 (m, 3H, H_{ar}), 6.88 (dd, 1H, J_{13} = 17.5; J_{23} = 10.9 Hz, H-3), 6.40 (m, 1H, H-et1,*cis*), 6.32 (m, 1H, H-et1,*trans*), 6.30 (m, 1H, H-et2,*cis*), 5.86 (m, 1H, H-et2,*trans*), 5.66 (dd, 1H, J_{13} = 17.5; J_{12} = 1.4 Hz, H-1), 5.26 (dd, 1H, J_{23} = 10.9; J_{12} = 1.4 Hz, H-2), 1.74 (m, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 136.32 (s), 135.98 (s), 135.18 (d), 132.06 (d), 131.30 (d),

130.10 (d), 128.08 (d), 127.24 (d), 127.14 (d), 126.24 (d), 125.47 (d), 115.23 (t), 18.32 (q). MS (EI) *m/z*: 170 (M^+, <2%), 128 (100). Anal. Calcd. for $C_{13}H_{14}$ (M_r = 170.25 g mol^{-1}): C, 91.71; H, 8.29%. Found: C, 91.37; H, 8.63%.

trans,*trans*-1-(*o*-Vinylphenyl)penta-1,3-diene (*trans*,*trans*-7a)

Colorless oil, (yield 28%). UV (EtOH) λ_{max}/nm (log ε /dm^3 mol^{-1} cm^{-1}): 287 (4.36), 249 (4.23). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.43 (m, 2H, H_{ar}), 7.20 (m, 2H, H_{ar}), 7.01 (dd, J_{13} = 17.5; J_{23} = 11.0 Hz, H-3), 6.70 (m, 1H, H-et1), 6.62 (m, 1H, H-et2), 6.26 (m, 1H, H-et3), 5.84 (m, 1H, H-et4), 5.60 (dd, 1H, J_{13} = 17.5; J_{12} = 1.4 Hz, H-1), 5.31 (dd, 1H, J_{23} = 11.0; J_{12} = 1.4 Hz, H-2), 1.82 (dd, 3H, J = 6.7; 1 Hz, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 135.56 (s), 135.24 (s), 134.54 (d), 131.61 (d), 131.08 (d), 130.01 (d), 127.23 (d), 126.73 (d), 126.66 (d), 125.98 (d), 125.33 (d), 115.64 (t), 17.83 (q). MS (EI) *m/z*: 170 (M^+, 100%). Anal. Calcd. for $C_{13}H_{14}$ (M_r = 170.25 g mol^{-1}): C, 91.71; H, 8.29%. Found: C, 91.37; H, 8.63%.

Thermal reactions – general procedure. A solution of *cis*,*trans*-**7a** (0.040 g, 0.24 mmol) was dissolved in toluene (25 mL) and refluxed for 25 h. Solvent was removed *in vacuo* and the oily residue was passed through a short silica gel column with petroleum ether. The thermal products, *endo*-**8a** and *exo*-**8a**, were best isolated by repeated column chromatography using petroleum ether as eluent, as a mixture of 33% *endo*- and 11% *exo*-isomer, based on ^{1}H NMR.

endo-7-Methyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (*endo*-8a)

Colorless oil, (yield 33%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.10–7.05 (m, 2H), 6.97 (dd, 1H, J = 6.6; 2.0 Hz), 6.88 (dd, 1H, J = 6.4; 1.9 Hz), 6.46 (dd, 1H, J = 9.9; 1.9 Hz, A), 5.77 (dd, 1H, J = 9.9; 3.6 Hz, B), 3.47 (dd, 1H, J = 18.0; 8.9 Hz, C), 3.29–3.24 (m, 1H, D), 2.98–2.89 (m, 1H, E), 2.38–2.32 (m, 1H, F), 1.99 (dd, 1H, J = 20.4; 10.5 Hz, G), 1.07 (d, 3H, J = 6.8 Hz, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 136.18 (s), 131.59 (s), 127.39 (d), 127.30 (d), 127.00 (d), 126.50 (d), 126.06 (d), 125.97 (d), 38.61 (d), 38.46 (t), 36.19 (d), 33.43 (d), 15.42 (q). MS (EI) *m/z*: 170 (M^+, <5%), 128 (100%).

exo-7-Methyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (*exo*-8a)

Colorless oil, (yield 11%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.10–7.05 (m, 2H), 6.97–6.93 (m, 2H), 6.29 (d, 1H, J = 9.8 Hz, A′), 5.85 (dd, 1H, J = 9.8; 4.4 Hz, B′), 3.70–3.66 (m, 1H, C′), 2.75–2.71 (m, 1H, D′), 2.49–2.41 (m, 2H, E′, F′), 2.09–2.04 (m, 1H, G′), 1.26 (d, 3H, J = 6.7 Hz, CH_3′). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 137.17 (s), 131.75 (s), 128.87 (d), 126.96 (d), 126.83 (d), 126.42 (d), 125.80 (d), 125.25 (d), 40.88 (d), 38.86 (d), 38.26 (t), 31.73 (d), 21.01 (q). MS (EI) *m/z*: 170 (M^+, <5%), 128 (100%). Anal. Calcd. for $C_{13}H_{14}$ (M_r = 170.25 g mol^{-1}): C, 91.71; H, 8.29%. Found: C, 91.95; H, 8.08%.

endo-7-Phenyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (*endo*-8b)

Colorless crystals. mp 79 °C, (yield 73%). UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 272 (2.67), 221 (4.33). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.28–7.36 (m, 3H), 7.20–7.24 (m, 2H), 7.09–7.11 (m, 2H), 6.95–6.98 (m, 2H), 6.34 (dd, 1H, J = 9.9; 2.0 Hz, H_A), 5.37 (dd, 1H, J = 9.9; 5.0 Hz, H_B), 4.10 (dt, 1H, J = 11.2; 7.7 Hz, H_E), 3.66 (m, 1H, H_D), 3.65 (dd, 1H, J = 17.9; 8.5 Hz, H_C), 2.82 (dd, 1H, J = 20.9; 11.2 Hz, H_F), 2.49 (m, 1H, H_G). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 140.03 (s), 136.07 (s), 132.20 (s), 128.00 (2d), 127.66 (d, C-A), 127.55 (d, C-B), 127.53 (2d), 127.30 (d), 127.06 (d), 126.77 (d), 126.59 (d), 126.09 (d), 45.78 (d, C-E), 41,60 (d, C-D), 34.62 (t, C-F,G), 33.64 (d, C-C). MS (EI) *m/z*: 232 (M^+, <5%), 128 (100), 104 (67). Anal. Calcd. for $C_{18}H_{16}$ (232.32): C, 93.06; H, 6.94%. Found: C, 92.91; H, 7.09%.

endo-7-Furyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (*endo*-8c)

Colorless crystals. mp 67 °C, (yield 56%). UV(EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 280 (2.54), 273 (2.77), 219 (4.23). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.34 (d, 1H, J = 1.1 Hz, H_{5f}), 7.05–7.11 (m, 2H), 6.96–6.99 (m, 1H), 6.92–6.95 (m, 1H), 6.39 (d, 1H, J = 10.1 Hz, H_A), 6.30 (dd, 1H, J = 3.1; 1.8 Hz, H_{4f}), 6.07 (d, 1H, J = 3.1 Hz, H_{3f}), 5.43 (dd, 1H, J = 10.1; 3.3 Hz, H_B), 4.04 (dt, 1H, J = 15.1; 7.8 Hz, H_E), 3.67 (m, 1H, H_D), 3.62 (dd, 1H, J = 17.9; 8.9 Hz, H_C), 2.73 (dd, 1H, J = 21.2; 10.8 Hz, H_F), 2.54 (m, 1H, H_G). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 155.57 (s), 141.16 (d, C-5f), 135.68 (s), 131.91 (s), 127.70 (d, C-A), 127.55 (d, C-B), 127.10 (2d), 126.78 (d), 126.57 (d), 109.98 (d, C-4f), 105,65 (d, C-3f), 41.22 (d, C-D), 39.30 (d, C-E), 34.67 (t, C-F,G), 33.76 (d, C-C). MS (EI) *m/z* 222 (M^+, <5%), 128 (100). Anal. Calcd. for $C_{16}H_{14}O$ (222.28): C, 86.45; H, 6.35%. Found: C, 86.62; H, 6.17%.

endo-7-Methyl-2,3-benzobicyclo[3.2.1]octa-2,5-diene (*endo*-11a)

A mixture of *cis*,*trans*-**7a** and *trans*,*trans*-**7a** isomers (0.170 g; 1.0 mmol) was dissolved in petroleum ether (130 mL) in a quartz photochemical vessel (c = 7,7 × 10^{-3} mol dm^{-3}). The solution was degassed by passing through a stream of argon for 20 min, and irradiated at 300 nm for 10 h. Solvent was evaporated under reduced pressure and the oily residue passed through a short silica gel column with petroleum ether. The photoproduct *endo*-**11a** was isolated and purified by repeated column chromatography using petroleum ether as eluent.

Colorless oil, (yield 26%). UV (EtOH) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 275 (2.82), 268 (2.84), 203 (4.14); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.19–7.16 (m, 1H, H_{ar}), 7.10–7.05 (m, 3H, H_{ar}), 6.09 (ddd, 1H, J_{AB} = 9.3; J_{AE} = 5.9; J_{AC} = 2.4 Hz, A), 5.02 (dt, 1H, J_{AB} = 9.3; J_{BC} = 2.3 Hz, B), 3.17 (m, 1H, C), 3.14 (t, 1H, J_{CD} = J_{DF} = 4.9 Hz, D), 2.68 (m, 1H, E), 2.42 (dt, 1H, J_{FG} = 9.8; J_{EF} = J_{DF} = 4.9 Hz, F), 2.15 (d, 1H, J_{FG} = 9.8 Hz, G), 0.83 (d, 3H, J = 7.4 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 135.33 (s), 142.56 (s), 132.70 (d), 129.47 (d), 126.23 (d), 125.91 (d), 125.43 (d), 120.41 (d), 46.83 (d), 43.76 (t, $C_{F,G}$), 40.70 (d), 34.59 (d), 18.07 (q). MS (EI) *m/z*: 170 (M^+, 100%), 115 (8%). Anal. Calcd. for $C_{13}H_{14}$ (M_r = 170.25 g mol^{-1}): C, 91.71; H, 8.29%. Found: C, 91.97; H, 8.03%.

Computational details

Geometrical optimizations and vibrational analyses were carried out employing the M06/6-31+G(d,p) computational method. Single point energies were further refined at the M06/6-311+G(d,p)//M06/6-31+G(d,p) level of theory. The connections between the reactants and the products were verified by intrinsic reaction coordinates (IRC) calculations. CPCM calculations were performed at the HF/6-31G* level (utilizing dielectric constant for

toluene $\varepsilon = 2.37$). Calculations were performed using *Gaussian03* and *Gaussian09* suite of programs,[35,36] implemented on dual core Opteron 240 personal computer under Linux operating system and computer cluster Isabella at the Computing center of the University of Zagreb (24 dual processor HP ProLiant BLP20p nodes with Intel Xeon 2.8 GHz, 32 dual processor Dell 1850 1U nodes with Intel Xeon 3.4 GHz and 24 dual processor Pyramid GX28 nodes with AMD Opteron 248). Harmonic vibration frequencies were calculated for all localized stationary structures to verify whether they are minima or transition states.

Acknowledgements

This research was funded by grants from the Croatian ministry of science, education and sports (125-0982933-2926, 098-0982929-2917, 098-0982933-3218 and 098-0982933-2920). The computing center of the Zagreb University is thanked for allocating the time at the computer cluster Isabella. We would also like to thank Dr Zoran Glasovac for valuable comments and discussion.

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