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Synthesis of a new photoresponsive molecular carcerand

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ABSTRACT

The synthesis of a covalently bonded new photoresponsive molecular capsule formed from two resorcin [4]arene cavitands by fourfold ether linkages using azobenzene subunits is reported. The new molecular capsule undergoes *trans* to *cis* isomerization upon irradiation with 365 nm light and can be reversed back from *cis* to *trans* form by means of exposure to visible light (530 nm) in benzene solution. The photoswitchable behaviour was also investigated by ¹H NMR spectroscopy which further substantiated the UV–vis experiment. The quantum chemical calculations both at PM6 as well as at the DFT (B97-D) level of approximation for various stereoisomers starting from all-*trans* to all-*cis* indicated an increasing flexibility of these molecular capsules.

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1. Introduction

The continuing growth in supramolecular chemistry for diverse applications such as molecular recognition and sensing, catalysis, cellular carriers and as biological mimics, demands highly sophisticated and larger molecular architectures. Therefore to expand the library of readily accessible and versatile organic molecular capsules, it is envisaged that a meticulous choice of resorcin[4]arene cavitands can often give highly symmetrical three dimensional cages through covalent bonding driven self-assembly processes. Early pioneering work by Cram and coworkers [1] has demonstrated the synthesis of carcerands and hemicarcerands, in which two resorcin[4]arene cavitands are held together by four covalent linkages attracting considerable attention for stabilizing reactive intermediates and for using them as microvesicles for drug delivery. Subsequently various recent examples were reported from the laboratories of Sherman [2], Warmuth [3], Kobayashi [4], and Rebek [5] on the diversified synthesis of resorcin[4]arene cavitands or capsules and their applications for host-guest interactions utilizing the fact that the confinement of guest molecules inside the capsules away from bulk phases may behave differently compared to their free form. However, the controlled

http://dx.doi.org/10.1016/j.jphotochem.2016.01.008 1010-6030/© 2016 Elsevier B.V. All rights reserved. encapsulation of guest molecules within the cavity of such molecular capsules is a great challenge and often depends on the flexibility of the linkers that bound the two cavitand units [6]. Earlier examples have employed various photoresponsive linker units where the molecular flexibility can be tuned by irradiation process at different wavelengths of light. For instance, our group has reported the synthesis of photoswitchable calixarenes and molecular capsules based on the photochemically driven dimerization of two anthracene moieties [7]. In a very recent example Wang et al. have reported on a reversible photochemically gated transformation of a hemicarcerand to a carcerand which is based on same concept of anthracene dimerization [8]. In another report calixarenes functionalized by other photoresponsive moieties such as acridinium and tropylium have been reported and found to be potentially useful for photoswitchable behavior [9].

Recent studies have demonstrated that the process of *trans-cis* isomerization of azobenzene also offers the possibility to control the flexibility and thereby geometry of molecules [10]. For example, Osorio-Planes et al. have reported on the reversible photocontrolled disintegration of a dimeric tetraurea-calix[4]pyrrole capsule with all*-trans* appended azobenzene units upon exposure to visible light [11]. Similarly Husaru et al. [12] and Yushkova et al. [13] have reported the synthesis of azobenzene substituted calix[4]resorcinarene and *p-tert*-butyl thiacalix[4]arene derivatives, respectively, where the cavity size of the molecules can be altered through the photoswitchable behavior of azobenzene units. In contrast to the first concept (i.e. cyclodimerization of anthracene units) the second

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Scheme 1. Synthesis of 4,4'-dihydroxyazobenzene (1).



Scheme 2. Synthesis of tetrabromo-resorcin[4]arene cavitand (4).

one utilizes a photoinduced isomerization process (*trans* to *cis* isomerization of azobenzene) leading to an altered geometry rather than covering/opening an entrance channel of a host compound. With this concept we now report the synthesis of a photoresponsive molecular capsule formed from two resorcin[4]arene cavitands by fourfold ether formation using azobenzene subunits as an example for covalently bonded molecular cavities with a "switchable wall". Its photochemical behavior as well as size dependence and flexibility on the *trans–cis* isomerization has been studied both experimentally and by quantum chemical calculations.

2. Results and discussion

The construction of the target molecular capsules involves the synthesis of functionalized cavitands. These cavitands will be further utilized to generate molecular assemblies by covalent bonding processes.

2.1. Synthesis and characterization

The synthesis of photoactive azobenzene linker **1** (Scheme 1) was achieved by diazonium coupling reaction of 4-aminophenol with phenol at 0 °C in 43% yield. Azo compound **1** is perfectly suited for the linkage to a resorcinarene via nucleophilic substitution reaction owing to its phenolic hydroxyl functions.

The octahydroxy resorcin[4]arene (**2**) was synthesized by acid catalyzed condensation reaction of 2-methyl resorcinol with *n*-pentanal in 73% yield. The cavitand formation was achieved by the treatment of **2** with bromochloromethane (BrCH₂Cl) in DMF with potassium carbonate as base under standard reaction conditions [14] to yield cavitand **3** in 92%. The complete bromination of the four methyl groups in **3** was performed with NBS in presence of AIBN to yield the functionalized building block **4** (55%) for the capsule synthesis (Scheme 2). The reaction between the resorcin [4]arene building block **4** and azobenzene linker **1** was performed



Scheme 3. Synthesis of the covalent molecular capsule (5).



Fig. 1. Variable temperature ¹H NMR spectra of **5** in CDCl₃ (a) -50 °C; (b) 0 °C; (c) +27 °C; (d) +50 °C.

in acetone with potassium carbonate as base under reflux condition to yield the dimeric capsule **5** (Scheme 3).

compared to our previous work whereby tedious purification step via HPLC could be avoided. As normal for this type of reaction the yield of the isolated product is rather low, since the formation of oligomer or polymer by-products is inevitable. However, MALDI

The dimeric capsule was directly obtained in one step instead of two or more consecutive reactions which is an advantage



Fig. 2. (a) ¹H NMR signal decays in dry CDCl₃ solution of 5 at 7.559 ppm at 293.3 K as a function of the diffusion gradient strength (G); (b) plot of signal decay as a function of the gradient strength (G).

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analysis of the crude product mixture obtained from the reaction of **4** and **1** showed a mass peak of the dimeric capsule whereas peaks corresponding to higher order molecular capsules were absent.

All compounds were characterized by means of NMR and high resolution mass spectrometry. Particularly the NMR spectra in CDCl₃ revealed that the symmetry of the resorcinarene core units is maintained in the dimer **5**. The aromatic protons of the resorcinarene core can be assigned to one singlet signal at 7.34 ppm corresponding to eight protons in the ¹H NMR spectrum of **5**. In addition the azobenzene units in **5** showed two distinct aromatic signals at 7.55 ppm and 6.59 ppm. Homo-nuclear coupling (COSY) between different aromatic protons further corroborated the complete analysis of the aromatic protons of the dimer molecule. The ¹H NMR results of **5** furthermore indicated that the azobenzene linkers are fixed symmetrically to each other.

Variable temperature NMR experiments were performed to study the flexibility of the dimeric capsule. ¹H NMR spectra were recorded in CDCl₃ at +50 °C, +27 °C, 0 °C and -50 °C (Fig. 1). Analysis of the protons signals of **5** at different temperatures exhibited almost no change in the chemical shift values of aromatic protons of the azobenzene linkers (at 7.55 ppm and 6.59 ppm) and the methylene bridge protons (at 5.73 ppm and 4.63 ppm) of the cavitands indicating the rigidity in the molecular structure. However the aromatic protons of the resorcinarene core (at 7.34 ppm) and lower rim alkyl proton (at 5.03 ppm) exhibited a slight upfield shift upon lowering the temperature from +27 °C to -50 °C possibly due to restriction of thermal motions at low temperature.

In addition, diffusion NMR spectroscopy provided useful data concerning the solution state of dimeric species. To the best of our knowledge diffusion NMR spectroscopy has been used only on aggregated species of resorcin[4]arenes, i.e. formed through noncovalent interactions [15]. In contrast, this is the first example where the particle size in solution has been estimated from the diffusion coefficient value of a covalently linked molecular capsule. We determined the diffusion coefficient of species existing in the NMR sample of **5** from the gradient diffusion of the aromatic signal at 7.559 ppm (Fig. 2) and found the coefficient value (D_t) to be 0.39×10^{-5} cm²/s at 293.3 K which is very close to the coefficient values obtained for other resorcinarene based self-assembled noncovalent dimeric aggregates [16].

2.2. Photochemistry

The absorption spectra of compounds 1 and 5 in degassed benzene solution are shown in Fig. 3. The capsule 5 showed a spectrum very similar to that of the azobenzene linker 1 which indicated the presence of symmetrical isomers of azobenzene units (Fig. 3a). The *trans-cis* isomerism study of the capsule **5** was performed at 365 nm and 530 nm wavelengths. Irradiation of 5 with 365 nm light for 30 min converted nearly all azobenzene units into cis-form as indicated by a decrease of the trans band and appearance of a new band at around 450 nm in the absorption spectrum (Fig. 3b). A photochemical reversion of the *cis*-isomer could be detected by irradiating the cis-5 with 530 nm light for 30 min as shown in Fig. 3b. An essential difference of the switching behavior occurs upon changing the solvent from benzene to chloroform. Conversion of trans-form to cis-form in 5 can be conducted in chloroform just as in benzene solvent by means of irradiation with 365 nm light, which was envisaged from the decrease of *trans* band in the absorption spectrum (Fig. 3c). Surprisingly the *cis*-form of **5** in chloroform could not be reversed to the trans-form either by irradiation with 530 nm light for 40 min or by keeping the sample in dark for overnight.



Fig. 3. UV–vis spectra of compound **5** and **1** (a), **5** in benzene (b) and **5** in chloroform (c), c = ca. 1 × 10⁻⁴ mol L⁻¹.

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Fig. 4. ¹H NMR spectra (in C₆D₆) of **5** in *trans*-form (a), after irradiation with 365 nm for 30 min (b) and after irradiation with 530 nm for 30 min (c). [red marked signal at 8.05 and 6.63 ppm for azobenzene aromatic protons]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The *trans–cis* isomeric conversion of **5** was also evaluated by NMR spectroscopy in deuterated benzene as solvent (Fig. 4a and b). A comparison of the ¹H NMR spectra of the *trans–* and *cis–*form indicated a change in the symmetry of the azobenzene units during the isomerization whereas the resorcinarene units are hardly disturbed. For instance, aromatic protons of the azobenzene units exhibited two broad doublets at 8.05 ppm and 6.63 ppm in the *trans–*form of **5** and upon irradiation with 365 nm light for 30 min these signals vanished completely and a series of doublets appeared at a slightly higher field similar to that observed for other azobenzene systems upon irradiation. Shifting signals to



Fig. 5. Calculated dimension of the all-trans azobenzene capsule (5).

high field can also be observed for the methylene bridged protons of the cavitand as well as for the methylene protons of the linkers (at 5.74 ppm, 5.48 ppm and 4.99 ppm in *trans*-form). However, the signal at 7.69 ppm, which can be ascribed to the aromatic protons of the resorcinarene phenyl units, was barely disturbed during the photochemical isomerization and indicated a symmetrical arrangement of the resorcinarene cores in the *cis*-form. The photochemical reversion of the *cis*-isomer was also investigated through NMR spectroscopy by irradiating the sample with 530 nm light for 30 min which showed reappearance of proton signals of the *trans*-form as shown in Fig. 4c.

2.3. Quantum chemical calculations

The calculated solvodynamic radius ($r_{\rm H}$) of the covalent molecular capsule using the diffusion coefficient value was found to be 9.6 Å. Preliminary calculations at the PM6 level showed that the azobenzene capsule exhibits an inner cavity of approx. dimension 8.6 Å × 22.1 Å (inter-atomic distances) (Fig. 5) which is very close to the inner cavity size of other resorcinarene based self-assembled non-covalent dimeric aggregates [17,18].

Further quantum chemical calculations of various structures of **5** were carried out at the DFT (B97-D) level of approximation and predicted the lowest energy for the structure with all -N=N- bonds having *trans*-configuration (Fig. 6a: **all-trans**). The starting geometries were preliminarily relaxed using molecular dynamics based on MM2 force field. As can be seen, the fully trans-structure is twisted, providing π,π -stacking and CH, π -interections with a participation of the aromatic rings of the aza-moieties. The all-*trans* structure is definitely most favorable, in complete agreement with the experimental data discussed above. The least favorable configuration is the structure with fully cis-oriented -N=N-

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Fig. 6. Jmol projections of equilibrium structures all-trans 5 and all-cis 5 and relative energy values (ΔG , kcal/mol).

fragment (Fig. 6b: **all**-*cis*) ($\Delta G = 62.0 \text{ kcal/mol}$ compared to **all**-*trans* **5**). In order to keep π,π -stacking and CH, π -interactions, the structure is folded in the region of the N=N-bonds. Both equilibrium structures correspond to local minima in energy, as can be concluded from absence of calculated imaginary frequencies.

Unfortunately, due to the large size of the molecule, it is extremely difficult to study computationally the **all-trans** \rightarrow **all-cis** transformation, but it might be suggested that this conversion proceeds gradually, with the inversion at only one nitrogen atom

per step. As our calculations indicate, the total (ΔE) and Gibbs free energy (ΔG) decrease smoothly from **all-trans** to **all-cis** via intermediate structures with increasing portion of cis-bonds (Fig. 7a–c). It should admitted here that the large size and conformational lability of the various structures of **5** do not allow to grant finding global minima in energy by geometry optimization even starting from the structures preliminarily relaxed using molecular dynamics. Therefore, in reality an equilibrium will exist within a variety of the structures with very close total energy. The



Fig. 7. Jmol projections of some equilibrium structures of **5** and relative energy values (ΔG , kcal/mol, related to **all**-*trans* **5**).

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Table 1

Calculated (RI-B97-D/TZVP) total energy values (*E*, Hartree), zero-point energy correction and thermal corrections to Gibbs free energy magnitudes (ZPE and TCGFE, Hartree), corrected energy values (*E*+ZPE and *E*+ TCGFE, Hartree), lowest vibrational frequency (ν , cm⁻¹) and corresponding relative energy values (ΔE and ΔG , kcal/mol).

Structure of 5	Ε	ZPE	E + ZPE	TCGFE	E+ TCGFE	ν	ΔE	ΔG
all-trans	-7180.717317	2.046531	-7178.670786	1.874828	-7178.842489	7.7	0.00	0.00
cis,trans,trans,trans	-7180.682355	2.046055	-7178.636300	1.873571	-7178.808784	7.4	21.6	21.2
cis,trans,cis,trans	-7180.657569	2.045452	-7178.612117	1.871210	-7178.786359	8.6	36.8	35.2
cis,trans,cis,cis	-7180.637654	2.044385	-7178.593269	1.870970	-7178.766685	27.3	48.6	47.6
all-cis	-7180.613068	2.044620	-7178.568449	1.869336	-7178.743733	7.0	64.2	62.0

optimized most favorable structures with an increasing number of cis-inversed N=N-bonds are shown in Fig. 7a-c (from *cis,trans, trans,trans* via *cis,trans,cis,trans* to *cis,trans,cis,cis*). The calculated total energy values for these structures seem to be intermediate cases between the fully *cis*- and *trans*-isomers (Table 1) and the structures themselves transform gradually from twisted to folded ones.

and host-guest type interactions can be envisaged inside the supramolecular system.

4. Experimental procedures

4.1. Synthesis of 4,4'-dihydroxyazobenzene (1)



3. Conclusions

In conclusion, the synthesis of a new macrocyclic capsule 5 based on two resorcin[4] arene units and four azobenzene linkers has been performed and the prepared compound was characterized by NMR and high resolution mass spectrometry. The new molecular capsule undergoes trans to cis isomerization upon irradiation with 365 nm light and can be reversed back from its cis to trans form by means of exposure to visible light (530 nm) in benzene. The photo-switchable behaviour of **5** was also investigated by ¹H NMR spectroscopy and further substantiated by the UV-vis experiment. To the best of our knowledge this is the first example of a covalently assembled molecular capsule with a "switchable wall" based on these units which can reversibly change its cavity by irradiation at different wavelengths of light. Since the geometry of the capsule and size of the cavity by the transformations from trans-form to cis-form and back to trans-form can be controlled by light, a number of interesting applications such as light driven chemical reactions

To a solution of 4-aminophenol (1.07 g, 9.81 mmol) dissolved in 1 N HCl solution (17.0 mL), a solution of sodium nitrite (1.13 g, 16.38 mmol), dissolved in 3.4 mL water was added dropwise at 0 °C with constant stirring. The mixture was diluted by adding pre-cooled to 0°C methanol (34.0 mL). In a separate flask, phenol (0.92 g, 9.78 mmol) and potassium hydroxide (1.04 g, 18.54 mmol, 1.9 eq) were dissolved in methanol (4.8 mL) and cooled to $0\,^\circ\text{C}$. This phenolate solution was added dropwise under constant stirring to the flask containing diazonium salt. The resulting red solution was stirred for additional 24 h. 1 N HCl solution was added to precipitate the crude product, which was collected by filtration. The crude product was then recrystallized from glacial acetic acid to give the product as a red-black solid (0.91 g, 4.25 mmol). Yield = 43%. ¹H NMR $(300 \text{ MHz}, \text{ acetone-} d_6) \delta \text{ ppm: } 6.97(d, 4H, J=9 \text{ Hz}), 7.77(d, 4H, J=9 \text{ Hz})$ I=9 Hz), 9.14(bs, 2H, D₂O-exchangeable). ESIMS (-ve): m/z for $[C_{12}H_{10}N_2O_2 + H2O + Na]^+$ Calcd: 255.07; found: 255.0.

4.2. Synthesis of tetramethyl resorcin[4]arene (2)



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10.28 g (82.8 mmol) of 2-methylresorcinol was dissolved in a mixture of 100 mL of ethanol and 50 mL of 37% aqueous hydrochloric acid (HCl). To this stirred solution 7.20 g (8.9 mL, 83.6 mmol) of *n*-pentanal was added slowly through a syringe. Immediately after the addition was complete, the reaction was cooled in a water bath to control the exothermic reaction. The reaction mixture was then maintained at 80 °C for 16 h, and the yellow solid that separated were collected and washed with cold 3: I ethanol–water mixture until the washings were light yellow. The pale colour solid material obtained was then dried at 80 °C under reduced pressure for 30 h. Yield = 73%. MP: > 230 °C (decomposed). precipitate obtained was filtered and washed repeatedly till the filtrate became neutral (controlled by pH paper). Then the solid product was recrystallized from chloroform and dried. Yield = 92%. MP: > 320 °C. ¹H NMR (500 MHz, CDCl₃) δ ppm: 0.92(t, 12H, J = 5 Hz), 1.34(m, 8H), 1.43(m, 8H), 1.97(s, 12H), 2.20(q, 8H), 4.25(d, 4H, J = 10 Hz), 4.74(t, 4H, J = 10 Hz), 5.88(d, 4H, J = 10 Hz), 6.98(s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ : 10.3, 14.1, 22.8, 29.7, 30.1, 36.9, 98.5, 117.5, 123.6, 137.9, 153.2, 162.5. EI-MS (+ve): m/z for [C₅₂H₆₄O₈] Calcd: 816.46; found: 816.5.

4.4. Synthesis of tetrabromo-resorcin[4]arene cavitand (4)



¹H NMR (500 MHz, acetone-*d*₆) δ ppm: 0.88(t, 12H, *J* = 5 Hz), 1.26 (m, 8H), 1.37(m, 8H), 2.04(s, 12H), 2.27(q, 8H), 4.35(t, 4H, *J* = 5 Hz), 7.43(s, 4H), 7.95(bs, 8H, D₂O-exchangeable). ¹³C NMR (125 MHz, acetone-*d*₆) δ: 10.7, 14.3, 22.6, 29.2, 35.4, 56.3, 113.6, 122.0, 124.6, 153.1.

4.3. Synthesis of resorcin[4]arene cavitand (3)

A mixture of cavitand **3** (0.0.498 g, 0.61 mmol) and AIBN (0.02 g, 0.12 mmol) were dissolved in 25 mL of benzene (deaerated by saturation with argon gas for 1 h). To this solution NBS (0.762 g, 4.28 mmol) was added and the reaction mixture was refluxed overnight (about 12 h) under argon atmosphere followed by TLC control. After completion of the reaction it was cooled, the solid succinimide precipitate was filtered off and the residue was washed with benzene (2×4 mL). The combined filtrate was



A mixture of dry resorcin[4]arene **2** (2.0 g, 2.6 mmol) and anhydrous K_2CO_3 (5.75 g, 41.6 mmol) in 60 mL of dry DMF was heated at 60 °C with stirring under argon (Ar) atmosphere for 30 min. Then CH₂BrCl (9.75 g, 75.35 mmol) was added to the reaction mixture in three fractions over a period of 40 h and after final addition of CH₂BrCl the reaction mixture was heated at 60 °C with stirring under argon (Ar) atmosphere for 12 h. After completion of the reaction, DMF was evaporated under reduced pressure and then water was added to the reaction mixture. The evaporated to get a pale white solid. The solid was dissolved in a small volume of acetone and then recrystallized from acetone by storing at low temperature to obtain a white solid. Yield = 0.38 g (55%). MP: > 300 °C. ¹H NMR (500 MHz, CDCl₃) δ ppm: 0.93(t, 12H, *J* = 5 Hz), 1.30(m, 8H), 1.44(m, 8H), 2.20(q, 8H), 4.42(s, 12H), 4.55(d, 4H, *J* = 5 Hz), 4.77(t, 4H, *J* = 10 Hz), 6.02(d, 4H, *J* = 5 Hz), 7.14(s, 4H). ¹³ C NMR (125 MHz, CDCl₃) δ : 14.1, 22.7, 22.9, 29.7, 30.0, 36.8, 99.1,120.9, 124.5, 138.0, 153.5. ESI-MS (-ve): *m/z* for [C52H60Br408 + H2O + 2Na]²⁺ Calcd: 1192.09; found: 1193.8.

4.5. Synthesis of the covalent molecular capsule (5)

Supplementary Information to this paper. The optimized structures were graphically represented using the Jmol program [27].



A mixture of 1 (0.047 g, 0.22 mmol) and anhydrous K_2CO_3 (0.61 g, 4.42 mmol) were taken in 125 mL of dry acetone and refluxed for 30 min. Then the reaction was cooled to room temperature and cavitand 4 (0.125 g, 0.11 mmol) was added and further refluxed for 12 h. After disappearance of starting tetrabromo resorcin[4]arene in the reaction mixture by TLC monitoring (9:1 cyclohexane and ethylacetate eluent) the reaction solvent was evaporated and 50 mL of chloroform was added to the residue. The suspension was filtered to remove the solid K₂CO₃ and the chloroform filtrate was washed with acidified 1N HCl solution followed by distilled water. The organic layer was separated, dried over anhydrous MgSO₄ and then evaporated under vacuum to yield a red coloured solid. This crude product was subjected to GPC purification in chloroform to obtain the desired azobenzene-linked molecular assembly. Yield = 11%. MP: > 300 °C. ¹H NMR (600 MHz, CDCl₃) δ ppm: 0.90–1.03 (m, 24H), 1.46–1.56(m, 32H), 2.36(q, 16H), 4.63(brs, 8H), 5.03(brs, 24H), 5.73(brs, 8H), 6.59(brs, 16H), 7.34(brs, 8H), 7.55(brs, 16H). ¹³C NMR (125 MHz, CDCl3) δ: 14.3, 22.9, 29.9, 30.3, 36.8, 60.4, 114.4, 121.9, 124.7, 128.9, 131.0, 138.7, 146.9, 154.5, 159.7. HRMS: m/z for $[C_{152}H_{152}N_8O_{24}+H]^+$ Calcd: 2475.10250; found: 2475.10279.

4.6. Details of calculations

All the structures were first optimized using the TURBOMOLE (versions 6.2 and 6.4) program packet [19] with the implemented Resolution Identity (RI) routine [20-23] and Multipole Accelerated Resolution of Identity J-algorithm (MARIJ) [24]. RI-B97-D functional [25] and standard triple-zeta basis sets (TZVP) [26] were used. The contraction of the basis functions were (11s6p)/ $[5s3p] \rightarrow \{62111/411\}$ for C, N and O, and $(5s)/[3s] \rightarrow \{311\}$ for H. One set of (five) d-functions was added for every non-hydrogen atom and one set of p-functions was used for H's. For all the structures vibrational analyses were performed, computing numerically first and second order derivatives. The absence of imaginary frequencies for the equilibrium structures proved that they were true local minima in energy. The corresponding zero point energy (ZPE) corrections and thermal corrections to Gibbs free energy (TCGFE) were derived at the RI-B97-D level of theory and used for calculations of ΔE and ΔG values with the default scaling. The complete calculation data set can be found in the

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem. 2016.01.008.

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