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Complete List of Authors:	Ramamurthy, V; Uni. Miami, Chemistry Sam Sunny, Amal; Uni. Miami, Chemistry
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An Organic Capsule as a Matrix to Capture and Store Reactive Molecules at Room Temperature in Aqueous Solution: 7-*cis*-β-Ionone

Amal Sam Sunny and V. Ramamurthy*
Department of Chemistry, University of Miami,
Coral Gables, Florida 33146, United States
Murthy1@miami.edu

Abstract

Low temperature matrix isolation method is the most popular one to generate and store reactive molecules and characterize them by in-situ IR spectroscopy. Recognizing the need for a simpler method to trap and store such molecules and characterize by NMR spectroscopy at room temperature in solution we have performed experiments exploring the value of water-soluble octa acid (OA) capsule as a storage vessel. The molecule we have chosen to illustrate the feasibility is the highly hindered 7-*cis*-β-ionone, which has been established to exist in equilibrium with its cyclic form with the later favored at room temperature. In this study we have shown that confined space can be an alternative to temperature to tilt an equilibrium towards higher energy isomer. During the course of the study, we were surprised to note that 7-*trans*-β-ionone aggregates in water and have distinct ^{1}H NMR spectra. Ability to assemble characterizable organic aggregates in water reveals the value of water as a reaction medium that is yet to be fully explored by photochemists. Finally, we have clarified the likely mechanism of secondary photoreaction of α-pyran to the final photoproduct that involves 1,5-hydrogen migration.

Introduction

Having made progress in establishing the value of confined spaces to control excited state chemistry and physics of molecules,(1-5) we became interested in exploring its value in trapping and storing reactive molecules at room temperature in solution. This goal was prompted by the pioneering studies of Cram and his co-workers in which they showed that highly reactive molecule such as cyclobutadiene could be stored at room temperature within a synthetic organic capsule.(6-9) We believed that this technique could complement the well-established low temperature matrix isolation technique that has been in use for several decades.(10-14) To begin with, in this study we have attempted to isolate and store the hindered 7-*cis* isomer of β-ionone within octa acid (OA) capsule (Figure 1) at room temperature in aqueous solution. Results of this exploration form the content of this presentation.

Figure 1.

Ionone skeleton plays an important role in a number of biologically relevant molecules such as retinal, vitamin-A, rhodopsin, bateriorhodopsin, carotene, etc. The ionone framework anchors molecule such as retinal into opsin protein allowing rest of the molecule to be flexible enough to undergo selective isomerization that serves to trigger a biological function such as 'vision'. Because of its biological relevance β-ionone and its higher members such as retinal have received considerable attention of photochemists and photophysicists, and synthetic, theoretical and bio-chemists as well as spectroscopists.(15-24) Of the various possible geometric isomers, 7-*cis* isomers are most hindered and their synthesis has been a challenge.(25-29) In fact, Pauling had predicted earlier that such isomers are too hindered to exist.(30, 31) However, this prediction was only short-lived. The first isomer in this category to attract the attention of two notable photochemists, Buchi and Yang was 7-*cis*- β-ionone (**2,** Scheme 1).(32) Because this molecule existed mostly in its cyclic form (α-pyran, **3**), formation of **2** as the product was unfortunately missed during the early photochemical investigation of 7-*trans*- β-ionone (**1**). However, a decade later presence of a small amount of **2** in the photoproduct mixture was realized by performing a careful study on thermal valence isomerization of **3**.(33, 34)

Scheme 1

It is obvious that if **2** is the primary photoproduct of **1** its isolation should be possible under conditions in which thermal conversion of the photoproduct **2** to **3** is unfavorable. One approach is to lower the temperature so that electrocyclization of **2** to **3** is prevented. In fact, two independent studies have spectroscopically identified **2** as a photoproduct when irradiation of **1** was conducted at low temperatures (in $CDCl_3$ at -50° C and in argon matrix at -263° C).(35-37) In $CDCl_3$ at –50° C the maximum amount of the 7-*cis* isomer formed was about 13%. With time this was converted (photochemically) to **3** and **4**.(38) Irradiation of **1** in argon matrix at –263° C although resulted in **4** as the final product at early stages there is evidence for formation of the 7-*cis* isomer. Thus although conversion of **1** to **2** has been established at low temperatures, up to now there is no clear evidence for its presence at room temperature.

Instead of temperature, we decided to utilize spatial confinement as a variant to isolate 7-*cis* isomer upon irradiation of **1**.(1) Based on our experience with photoreactions within various hosts, we anticipated that 6*e*-electrocyclization of **2** would be hindered within the confined space of OA capsule. With this in mind we have carried out photochemical study of host-guest complex of **1** with OA (the inclusion complex is represented as **1**@OA_2). Interestingly, within OA capsule even at room temperature, **2** is the major product as characterized by ^{1}H NMR. At 2.5° C where conversion to **3** is significantly slowed, presence of **2** in the product mixture was about 70%. Apparently, the reduced space increased the barrier for conversion of **2** to **3**. The observation made with the hindered **2** provides encouragement for future use of OA capsule to trap reactive molecules.

Interestingly while preparing the host-guest complex of **1** with OA in borate buffer we were surprised to detect duplicate and triplicate NMR signals for **1** in water. To the naked eye although the solution remained transparent, ^{1}H NMR spectra revealed the presence of multiple signals for each hydrogens of the monomer suggesting that there are various forms of **1** in solution. Through diffusion constant measurement with DOSY-NMR and particle size by dynamic light scattering experiments we have established the signals to be due to different sized aggregates of **1** in water. Details of this study are also presented below. Finally, upon examination of the ionone literature we came across a report on direct formation of **4** from excited **3** via an usual 1,5 H migration (Scheme 2).(37, 36) Given that **3** exists in equilibrium with **2** it seemed more probable that the reaction proceeded from **2** rather than **3** *via* the proposed mechanism. Although it was a detour from the original goal, we thought that it is worth establishing the origin of the final photoproduct of **1** in solution. Results of this investigation are also summarized below.

Scheme 2

Materials and Methods

General Information: Commercially available materials were used as supplied without purification, unless specified. ^{1}H-NMR characterization, NMR titration studies and 2D ^{1}H-NMR (COSY) experiments were performed on Bruker Avance 500 spectrometer equipped with cryoprobe. Diffusion experiments were performed on Bruker Avance 400 spectrometer. Variable temperature experiments were carried out by changing the temperature of the NMR probe. Chemical shifts are reported in parts-per-million (ppm). Deuterated solvent was used as a lock and residual protonated solvent peak was used as reference. Absorption spectra were recorded on a Shimadzu UV-3150 spectrophotometer. Dynamic Light Scattering (DLS) measurements were recorded on a Malvern zetasizer nano.

Materials: Octa Acid (OA) was synthesized according to the reported procedure.(39) *Trans*-β-ionone from Aldrich was purified by silica gel column chromatography. α-Pyran was obtained by irradiation of *trans*-β-ionone (2 g) in cyclohexane (50 mL) with medium pressure mercury lamp at room temperature for 24 hours and purified by silica gel column chromatography, using a 3% (v/v) mixture of ethylacetate and hexane as eluent. Product (500 mg, 25%) was characterized by ^{1}H-NMR.

General Protocol for Complexation Studies: A 60 mM stock solution of the guest was prepared in DMSO-d$_6$. Appropriate amount of this stock solution was added to a 1 mM solution of OA (in 10 mM borate buffer in D$_2$O) such that 0.25 equivalents of guest were added upon each addition. Complexation was achieved by shaking the NMR tube and spectra were recorded at room temperature.

Irradiation at room temperature: The samples were taken in NMR tubes and were degassed by purging with N_2 for 20 minutes. These samples were then irradiated in a Rayonet reactor fitted with eight RPR-3000 lamps. The irradiated samples were analyzed by ^{1}H-NMR.

Irradiation at 77 K: The samples were taken in an NMR tube and were degassed by purging with N_2 for 20 minutes. The NMR tube was then inserted into a transparent Dewar vessel filled with liquid N_2. These samples were then irradiated in a Rayonet reactor fitted with eight RPR-3000 lamps while keeping the NMR tube in liquid N_2. After irradiation, the sample was thawed, and the ^{1}H-NMR spectra were recorded.

Diffusion Experiments: Diffusion NMR studies of **1**@OA$_2$: A 1:2 complex of **1** and OA (1 mM of **1** and 2 mM of OA) was prepared in 20 mM D_2O buffer. Diffusion experiments were carried out to characterize the capsular assembly.

Diffusion NMR studies of monomers and aggregates of ***1***: A 150 mM stock solution of **1** was prepared in DMSO-d$_6$. Aliquot (10 µL) of this stock solution was added to 600 µL D_2O to give 2.5 mM of **1** in D_2O. Diffusion experiments were carried out to characterize the monomers and aggregates.

UV-Visible Absorption Spectra: A 60 mM stock solution of **1** was prepared in DMSO-d$_6$. Appropriate amount of this stock solution was added to deionized water and the UV spectra were recorded at different concentrations of **1**.

Dynamic Light Scattering (DLS) Experiments: A 500 mM stock solution of **1** was prepared in DMSO-d$_6$. Appropriate amount of this stock solution was added to triple distilled water and the DLS measurements were carried out at various concentrations of **1**.

Results

Octa acid (OA), although insoluble in neutral water, dissolves in borate buffer solution remaining as monomer till 1 mM and as aggregates above it.(40) Therefore all experiments were carried out as borate buffer solutions. To examine the thermal and photochemical behavior of **1** in a constrained space the host-guest complex of **1** within the OA capsule was prepared by stirring a known amount of **1** with 1 mM borate buffer solution of OA. The formation and nature of the complex were confirmed by ^{1}H NMR spectra. Titration of **1** into 1 mM borate buffer solution of OA was carried out by slow addition of guest **1** into OA in an NMR tube. ^{1}H NMR spectra of samples containing various ratios of **1** and OA are displayed in Figure 2. It is important to note that the guest signals are significantly upfield shifted in presence of OA. Methyl signals of **1** appearing below δ 0 ppm is significant. Individual ^{1}H NMR spectra of **1** in DMSO-d_6 and the complex in borate buffer (D_2O) where signals are assigned by COSY experiments are provided in Figure 3(for COSY see Figures S1 and S2). Upon comparison of the two spectra large upfield shift of the guest signals is clearly evident. Such upfield shifts upon inclusion within the OA capsule has been established with a number of guest molecules.(40, 41) Based on these we believe that the chemistry of **1** we report here occurs within the confined space of the OA capsule.

The host:guest ratio was deciphered by close examination of the host signals in various spectra. The bottom most trace in Figure 2 corresponds to free OA. Upon addition of **1** to the host solution, new signals in addition to the signals due to uncomplexed free OA appear for the host protons in the region δ 5.8–7.8 ppm. No further changes in the OA signals are noticed beyond addition of 0.5 mM of **1** to 1 mM OA. At this stage all free OA signals were replaced with new signals due to the complex. In fact, further addition resulted in signals due to free **1** in water (see the region δ 1–2 ppm in trace vi in Figure 2). These suggested that the guest **1** forms a 2:1 host-guest capsular complex. Decreased diffusion constant for the complex ($1.36 \pm 0.095 \times 10^{-10}$ m^2/s) with respect to the guest alone (5.28×10^{-10} m^2/s) measured by DOSY experiments supported this conclusion (Figure S3 and S4 and Table S1).(41, 40)

Figure 2

Figure 3

To pursue the main goal of this investigation namely to assess the stability of *cis*-β-ionone (**2**) within the OA capsule we carried out irradiation of 2:1 host-guest complex in a NMR tube with 310 ± 25 nm light (Rayonet reactor fitted with RPR-3000 lamps). The products were identified by their characteristic ^{1}H NMR signals and the percentages were estimated by integrating the corresponding signals (see also Figure S5, S6 and S7). As per NMR spectra upon irradiation, **1** was transformed to **2** and **3** (Scheme 1 and Figure 4b; also see Figures S7-S9). Small amounts (< 5%) of oxygen addition product **5** (Scheme 1) and hydrogen migration product **4** (Scheme 1) also were formed but these were not taken into account in Figure 4 where the time evolution of the products in DMSO-d_6 and within the OA capsule are plotted. In DMSO-d_6 solution at room temperature the *trans*-isomer is converted to the *cis* and even at early times α-pyran **3** is present along with **2**. In an hour of irradiation, 50% of **1** is converted to a mixture of **2** and **3**. As seen in Figure 3(a) in DMSO-d_6 solution the major product at room temperature is α-pyran **3**. Interestingly, within the OA capsule the photoreaction was faster and the amount of the *cis*-isomer formed was much higher: (a) Within the capsule 50% conversion was reached in 8 mts while in DMSO-d_6 it took 60 mts. (b) Most importantly, the % of *cis* at 50% conversion within the OA capsule was 42% while that in DMSO-d_6 solution was 12%. The above results clearly brings out the important role the confined space plays during photoisomerization of β-ionone derivatives.

Figure 4

Generally, formation of **3** from **1** is believed to occur via the isomer **2**. While the first step (geometric isomerization) is photochemical, the second step namely electrocyclization is presumed to be a thermal process. At normal temperatures, the primary photoproduct **2** immediately cyclizes to the more stable isomer **3**. It is not obvious whether this would be true even in a confined environment. To probe the role the confined space plays on this thermal cyclization, a mixture of **2** and **3** (80 and 20%) prepared by irradiation of **1** at 2.5° C was kept at this temperature for several hours and the ratio with respect to time was followed by ^{1}H NMR. As seen in Figure 5 in solution it reached an equilibrium containing 28% **2** and 72% **3** in about 5 hour. On the other hand, within OA capsule in the same time scale the mixture contained 70% **2** and 30% **3**. We believe this suggests that there is an enhanced barrier for cyclization of **2** within the OA capsule.

Slow cyclization of **2** to **3** within OA capsule rises a question whether formation of **3** within the capsule is the result of a secondary thermal or photochemical process. To test this we carried out irradiation of **1**@OA$_2$ in borate buffer frozen at 77 K. The buffer remained as opaque ice at this temperature and most likely the photoreaction occurred at the first few layers of ice. We visualized that at 77 K thermal cyclization would be prevented. However, upon irradiation of **1**@OA$_2$ the isomerization still occurred with 44% conversion in 20 mts to yield a product mixture containing 32% **2** and 24% **3**. This observation led us to conclude that **3** can also be formed via photochemical route within OA capsule at low temperatures. In $CDCl_3$ solution only 10% conversion was achieved even after 6 hours of irradiation. As expected in frozen $CDCl_3$ without free space around the reactant molecule no isomerization occurred. Apparently, within the capsule the free space not subjected to compression by adjacent molecules allows excited guest molecules to undergo cyclization.

Figure 5

As we perused the literature on the photochemistry of **1** we noticed that excited **3** is proposed to give **4** via an unusual 1,5 H-migration (Scheme 2). Since at room temperature **3** exists in equilibrium with **2** formation of **4** via the conventional 1,5 H-migration from **2** seemed more likely than direct conversion of **3** to **4**. To rule out the unlikely possibility of direct photoconversion of **3** to **4** we closely followed the product formation at initial stages of irradiation of **3** in DMSO-d_6 at 25° C and 77 K. As shown in Figure 6 at both temperatures the primary photoproduct at very early stages of irradiation (<10 mts) is the *cis* isomer. Product **4** seemed to appear after the accumulation of **1** and **2**. This is much clearer in the samples where irradiation is conducted at 77 K (Figure 6b). Based on the plots shown in Figure 6 we conclude that **3** does not undergo direct photoconversion to **4** as outlined in the literature. Most likely as outlined in Scheme 3 both *cis* and *trans* isomers of β-ionone upon excitation yield **4** via Woodward-Hoffmann allowed 1,5 H-migration.

Scheme 3

Figure 6

The final observation relates to the unusual phenomenon we noted when **1** was dispersed in borate buffer to prepare the OA-guest complex. In Figure 7 the ^1H NMR spectra at various concentrations of **1** in water are presented. At 1 mM solution in D_2O the expected signals for **1** were recorded and all could be assigned based on comparison with ^1H NMR in DMSO (Figure 2). However as the concentration was increased another set of signals due to **1** was clearly seen. As the concentration was varied between 1 to 5 mM the ratio of the original to the ‘qdditional signals changed in favor of the latter (note starred peaks in Figure 7). Interestingly, the second set of signals were seen for every hydrogens present in the molecule. We believe the second set of signals is due to aggregation of **1** in water. At higher concentrations, weak third and fourth set of signals were visible in the spectra (note amplified insert in Figure 7 for 5 mM solution). We suspected these signals to derive from aggregates. To confirm the presence of aggregates dynamic light scattering experiments were carried out. According to DLS measurements the average size of the aggregates varied between 182.1 nm and 1159.0 nm as the concentration was changed between 0.5 and 4 mM. Interestingly, there was a gradual increase in the size of the aggregates: 0.5 mM: 182.1 nm; 1.0 mM: 275.2 nm; 2.0 mM 723.7 nm; 3 mM: 912.9 nm and 4.0 mM: 1159.0 nm (Figures S10-14 and Table S12). Although there were new NMR signals for the aggregates there was no change in the absorption spectra with respect to concentration (Figure S15). This suggested that there is no order in the aggregates to influence the electronic transitions. The diffusion constants of the monomer and aggregates differed as measure by NMR DOSY experiments. As expected the aggregates had lower diffusion constants (0.64×10^{-10} m^2/s) than monomer (5.28×10^{-10} m^2/s) (Table S1). Interestingly, **1**@OA_2 capsule diffuses (1.36×10^{-10} m^2/s) slower than monomer and faster than aggregates. To our knowledge this is a distinctive example of an organic molecular aggregate that could be characterized by NMR, DLS and diffusion constants.

Figure 7

Finally having noticed that **1** exists as an equilibrium mixture of monomer and aggregates we were curious to find out whether there is any preference between the monomer and aggregates to complex with OA. Given the size of the aggregates one would expect the monomer to get included within OA first. The NMR spectra presented in Figure 9 show that this is the case. Upon addition of OA to a solution of **1** that exists as monomer–aggregate mixture the monomer signals disappeared at early stages indicating that monomer complexed to OA first. With time the signals due to aggregates also decreased indicating these were converted to monomer and the latter complexed to OA. Overall the detection of the presence of aggregates of

1 in water by NMR is significant. At this stage we don't fully understand the origin of the upfield shift in the NMR signals due to aggregates.

Figure 8

Discussion

We undertook the current study with the primary goal of establishing the value of organic capsules as a vehicle to trap and store reactive and high-energy molecules at room temperature in solution. We visualized this technique could become a complement to the well-known low-temperature matrix isolation method.(13, 14, 11) To our knowledge since the early ground breaking studies by Cram and co-workers not much progress has been made on this front.(6) This is likely to be due to the non-availability of water-soluble, light transparent and inert capsules that would hold large guest molecules.(42) A few years ago we showed that a high energy conformer of a piperidine derivative could be trapped within the OA capsule.(43) This gave us encouragement to look for systems that are less stable in solution that could be preserved within OA capsule. This led us to 7-*cis*-β-ionone that is long known to be highly hindered (30, 31), difficult to accumulate and thermodynamically less stable than its valence isomer α-pyran **3**. Elegant studies by Marvell and his co-workers have established that **2** and **3** exists in thermal equilibrium in favor of **3** at room temperature.(33, 34) Since cyclization of **2** to **3** requires considerable space we felt that this process will be slowed or arrested in an environment where there is lack of free space.(5) Octa acid with restricted interior space (Figure 9), we surmised would be an ideal environment to stop/slow the conversion of *cis* to a cyclic product.

Figure 9

Results presented in Figures 2 and 3 have established that **1** forms 2:1 (host:guest) complex in solution. Results shown in Figure 4 hint that geometric isomerization of OA encapsulated **1** is faster than in an isotropic DMSO solution. Although geometric isomerization requires considerable amount of free space for one part of the molecule to make a 180° sweeping motion the fact that it occurred faster within the capsule than in solution suggests that most likely the *trans* isomer is not comfortably placed (i.e., bound weakly) within the capsule. It seems that upon activation with light, it quickly flipped to the more hindered *cis*-isomer that probably fits better within the OA capsule. We have observed similar occurrence in substituted stilbenes where the photostationary state was in favor of the isomer that fitted better within the OA capsule.(44) The current observation also supports the general conclusion that the chemistry of host-guest complexes should be understood on the basis of supramolecule rather than a single molecule.(45) The fact that 7-*cis* isomer is present in larger amounts, at least during the initial stages of irradiation, within capsule suggests that the second thermal step namely cyclization has a higher barrier within the capsule than in solution. It is interesting to note that while the geometric isomerization that sweeps much larger volume is allowed within the confined space of the OA capsule, the cyclization that requires smaller free space is hindered.

The plot of product distribution with respect to time for a sample prepared by irradiation and kept at 2.5° C shown in Figure 5 clearly indicates that within the OA capsule the 7-*cis* has a higher barrier to cyclize than in solution. It can be seen in the figure that ~80:20 mixture of *cis* and α-pyran reaches an equilibrium of 28:72 (*cis* and α-pyran) in 5 hours while for the same length of time there is only slight change within OA capsule. Thus, accumulation of 7-*cis* within OA capsule can be attributed to the barrier imposed on the thermal cyclization by the capsular interior.

One of the unanticipated observations during this study was the identification of aggregates of **1** in aqueous solution. Not only presence of aggregates could be characterized by DLS and diffusion constant measurements, NMR spectra which looked very similar to monomers at very low concentrations could be recorded. Since the aggregates and monomer have identical absorption spectra we believe that these aggregates have no well-defined organized structures (Figure S15). In any case, ability to solubilize hydrophobic organic molecules in water provides an opportunity to examine their chemistry in water, a less explored topic. Thus our exploration to establish the value of organic capsules as a vessel to store reactive molecules has opened an opportunity namely to explore water as a reaction medium.(46-51)

Conclusions

Hindered 7-*cis*-β-ionone formed upon photoisomerization is stable within the OA capsule. Conversion to the more stable isomer via electrocyclization is slowed by the capsule with little free space. This observation hints at the value of the OA capsule to store energy-rich and highly reactive molecules. We plan to pursue this aspect of 'container chemistry' in the future. While there is considerable literature on organic nanoparticles especially of aromatic molecules in conventional solvents, to our knowledge no such aggregates have been reported for common organic molecules in water. We have demonstrated that molecules such as 7-*trans*-β-ionone exists as aggregates in water. This observation opens up opportunities to pursue photochemistry of organic molecules in water.

Author information

V. Ramamurthy, Orcid # 0000-0002-3168-2185; email: murthy1@miami.edu
Amal Sam Sunny, Orcid # 0000-0003-3440-3636; email: axs3024@miami.edu

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Supporting Materials

Additional supporting information may be found online in the Supporting Information section at the end of the article:

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List of Figure legends

Figure 1. Top: Structure and dimensions of cavitand octa acid. Bottom: CPK model of the capsular assembly of two molecules of octa acid

Figure 2. ^{1}H-NMR (500 MHz, D_2O) spectra of (i) 1 mM OA in borate buffer (ii) **1**@OA ([OA] = 1 mM, [**1**] = 0.125 mM), (iii) **1**@OA ([OA] = 1 mM, [**1**] = 0.25 mM), (iv) **1**@OA ([OA] = 1 mM, [**1**] = 0.375 mM), (v) **1**@OA ([OA] = 1 mM, [**1**] = 0.5 mM), (vi) **1**@OA ([OA] = 1 mM, [**1**] = 2.5 mM); "•" represents residual D_2O.

Figure 3. ^{1}H-NMR (500 MHz) spectra of (a) **1** in DMSO-d_6 (* & * represent residual DMSO and HOD peak in DMSO-d_6 respectively), (b) **1**@OA_2 in buffered D_2O ("•" represents residual D_2O and the OA protons are labelled a to g).

Figure 4. (a): Time dependent product distribution upon irradiation (310 ± 25 nm light; Rayonet reactor fitted with RPR-3000 lamps) of **1** at room temperature in DMSO-d_6 solvent. (b): Time dependent product distribution upon irradiation of **1**@OA_2 in buffered D_2O at room temperature. Both in solution and within OA capsule products formed in less than 5% (*retro*-γ-ionone **4** and the oxidation product 1, 2, 4-trioxane **5**) were not taken into account in the plot. Note the % of *cis* isomer is much higher within capsule.

Figure 5. (a): Monitoring the thermal conversion of **2** to **3** (a) in solution and (b) within OA capsule at 2.5° C. The initial mixture was prepared by irradiation of **1**. For the plot only **2** and **3** are considered. The unreacted **1** is not taken into account.

Figure 6. Product distribution with respect to time of irradiation (310 ± 25 nm light; Rayonet reactor fitted with RPR-3000 lamps) in DMSO-d_6 (a) at 25° C and (b) at 77 K. Oxidation product **5** formed in less than 5% was not included in the product distribution. Note the absence of **5** at early stages of irradiation, this is much clearer at 77 K.

Figure 7. ^{1}H-NMR (500 MHz, D_2O) spectra of **1** at various concentrations; (i) 1 mM, (ii) 2 mM, (iii) 3 mM, (iv) 4 mM and (v) 5 mM. The aggregate signals are labelled with *. The insert (trace

vi) shows the higher order peaks. Signals corresponding to higher order aggregates are marked with * and *.

Figure 8. Partial ^{1}H-NMR (500 MHz, buffered D_2O) spectra upon addition of OA to a solution of **1** in borate buffer (D_2O). (i) 2.5 mM **1**, (ii) 2.5 mM **1** + 0.5 mM OA, (iii) 2.5 mM **1** + 1 mM OA, (iv) 2.5 mM **1** + 1.5 mM OA, (v) 2.5 mM **1** + 2 mM OA, (vi) 2.5 mM **1** + 2.5 mM OA, (vii) 2.5 mM **1** + 3 mM OA, (viii) 2.5 mM **1** + 3.5 mM OA, (xi) 2.5 mM **1** + 4 mM OA and (x) 2.5 mM **1** + 5 mM OA. The aggregate signals are indicated by *. Signals corresponding to bound **1** are marked as *.

Figure 9. A cartoon presentation of the cavity of the cavitand OA. Entrance diameter and depth of the cavity presented.

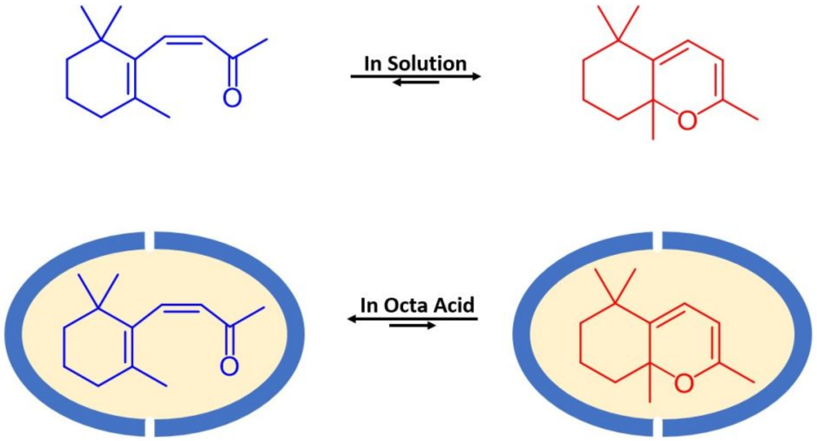
Captions for Schemes

Scheme 1: Products of direct and triplet sensitized excitation of *trans*-β-ionone (**1**) in solution. Isomers **2** and **3** are shown to be in equilibrium.

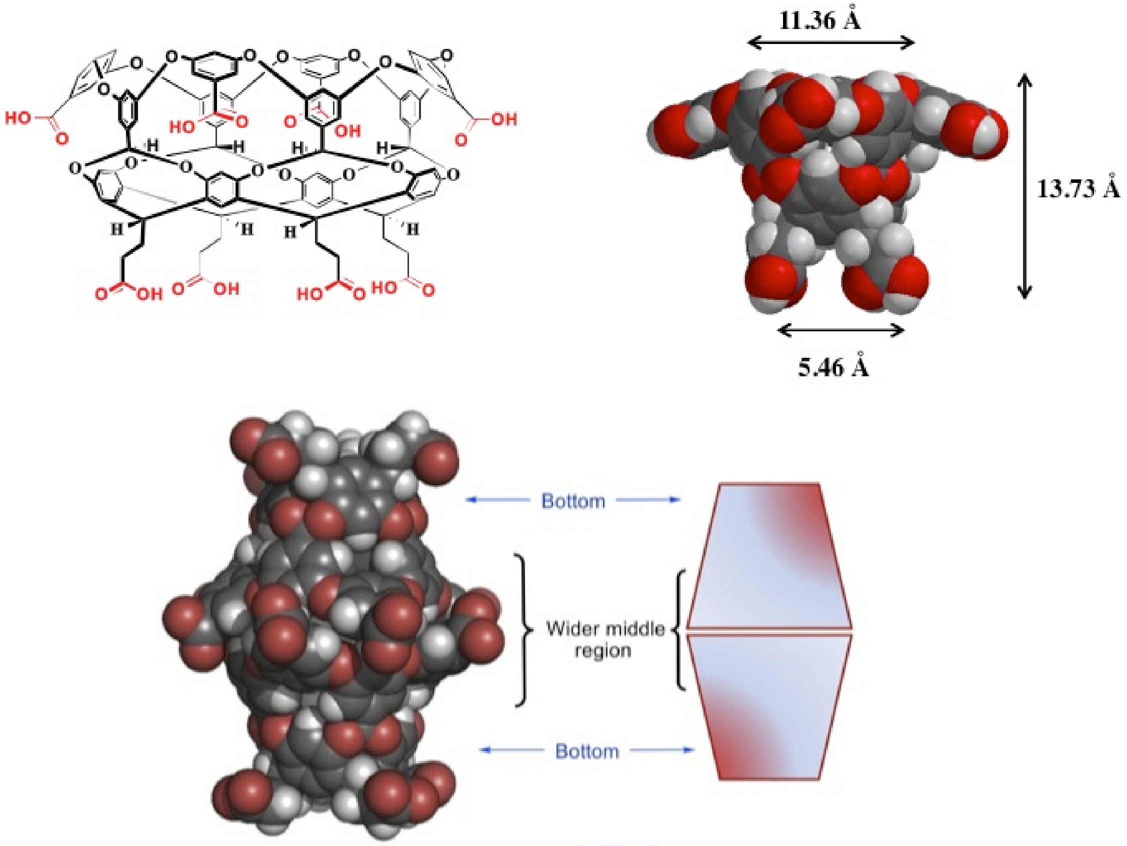
Scheme 2: Proposed mechanism in the literature for formation of **4** from **3** upon direct excitation.(36)

Scheme 3. Proposed mechanism for the formation of **4** from excited **3**.

TOC Graphics and Abstract



Fascination to store and handle exotic, high energy and strained molecules has not subsided with time. The most popular method in this context is the low temperature inert gas matrix isolation spectroscopy. While this method has brought revolution in preparing and characterizing highly unstable organic and inorganic molecules at very low temperatures (< 20 K), a simpler method with the ability to trap and store above type of molecules at room temperature would be exceptionally useful. Following the footsteps of Cram we have explored the value of octa acid capsule to store reactive and/or strained molecules.



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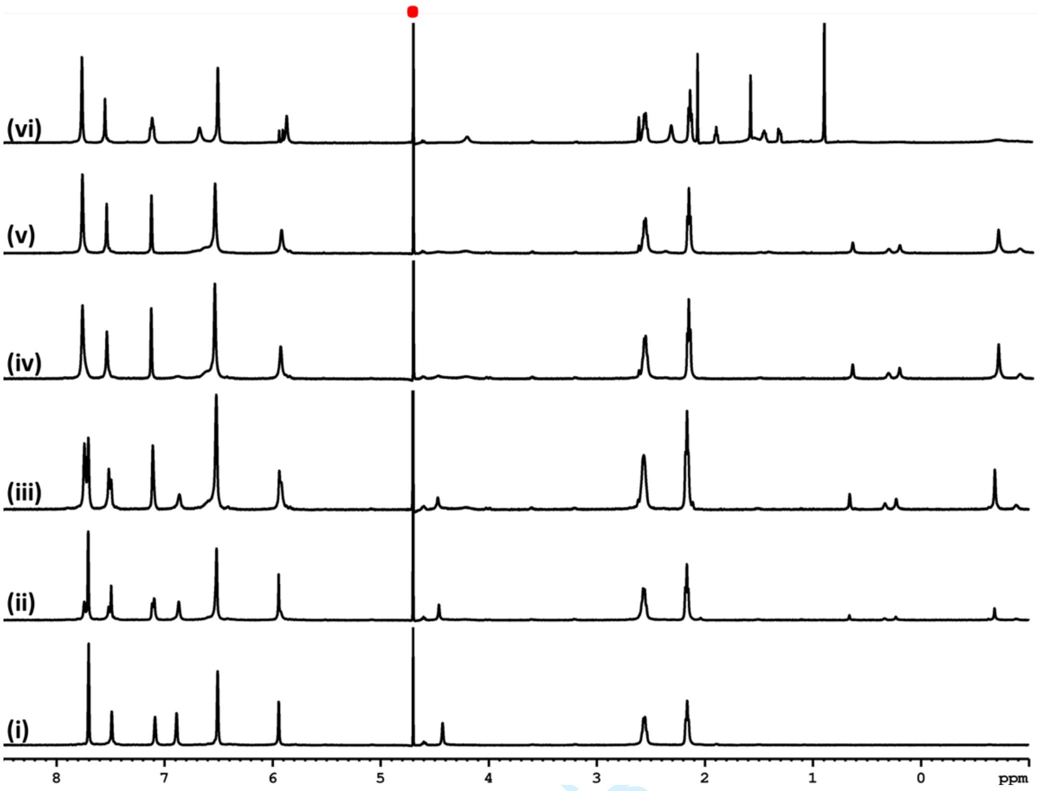

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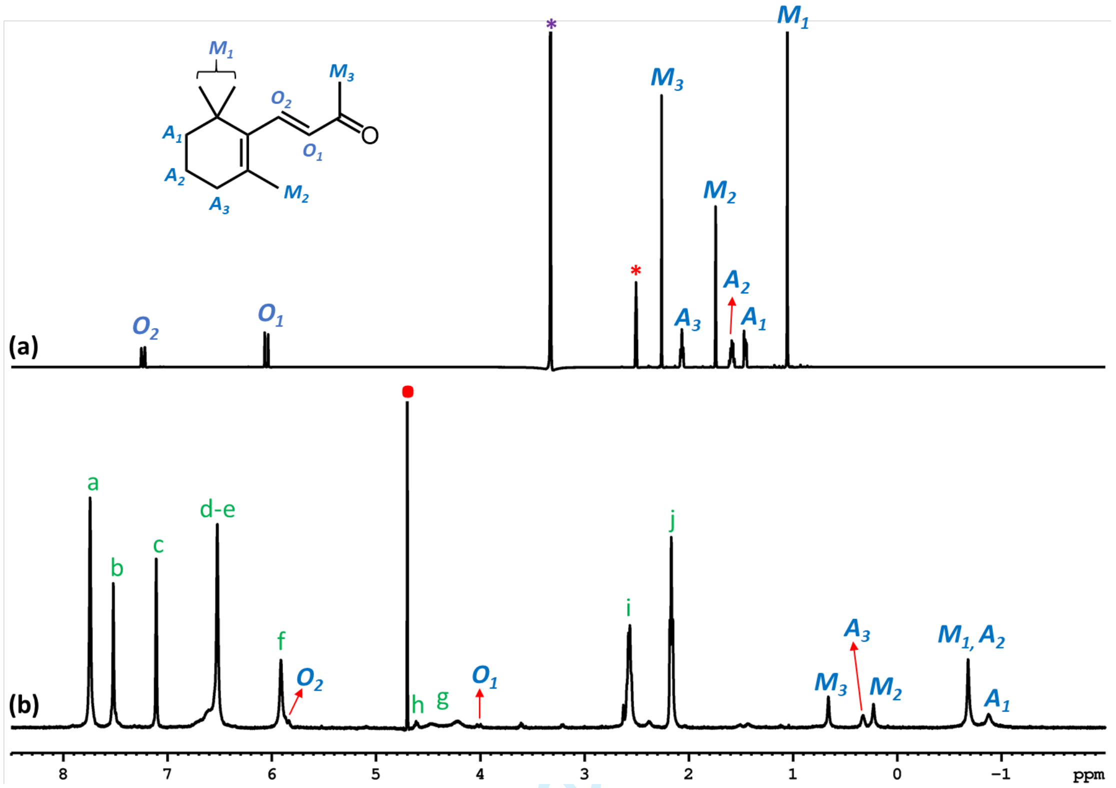
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c
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g
O_1
i
j
A_3
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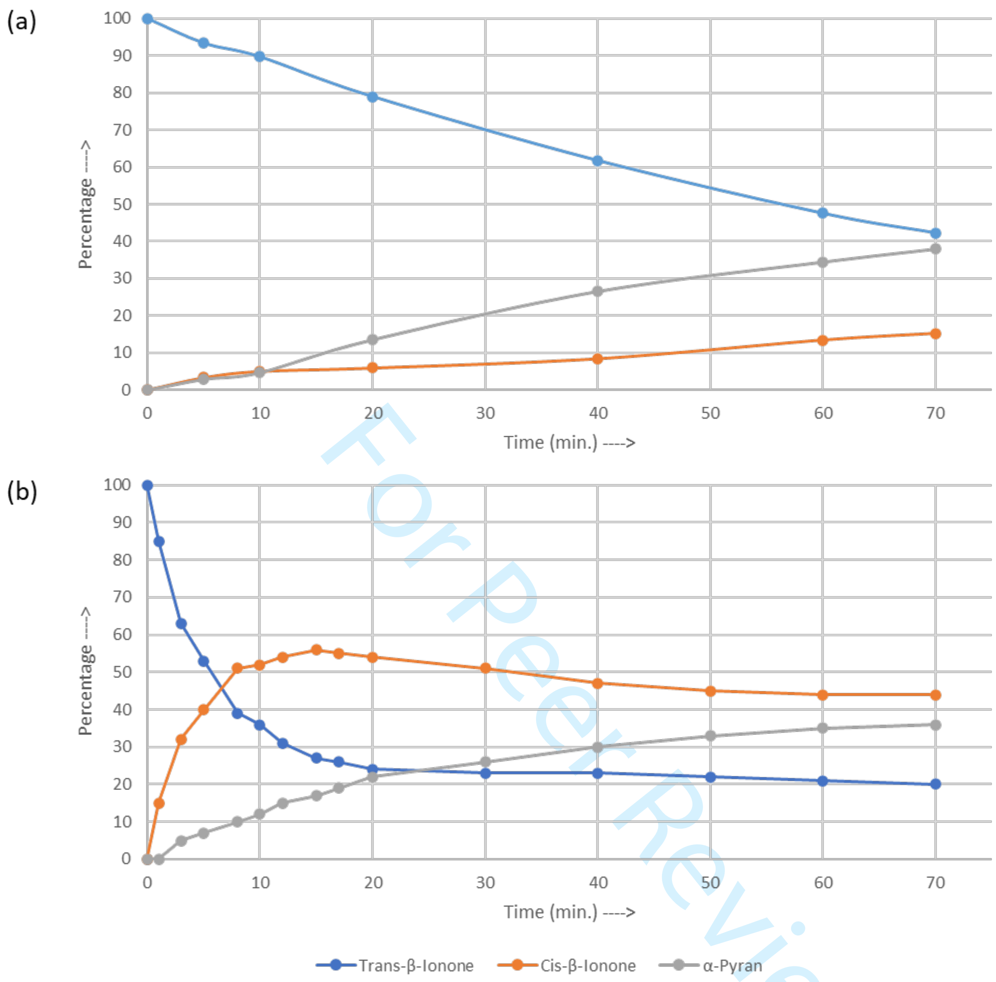
−1
ppm

Figure 3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50
60
70
Time (min.) ---->
(b)
Percentage ---->
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80
70
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50
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30
20
10
0
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Time (min.) ---->
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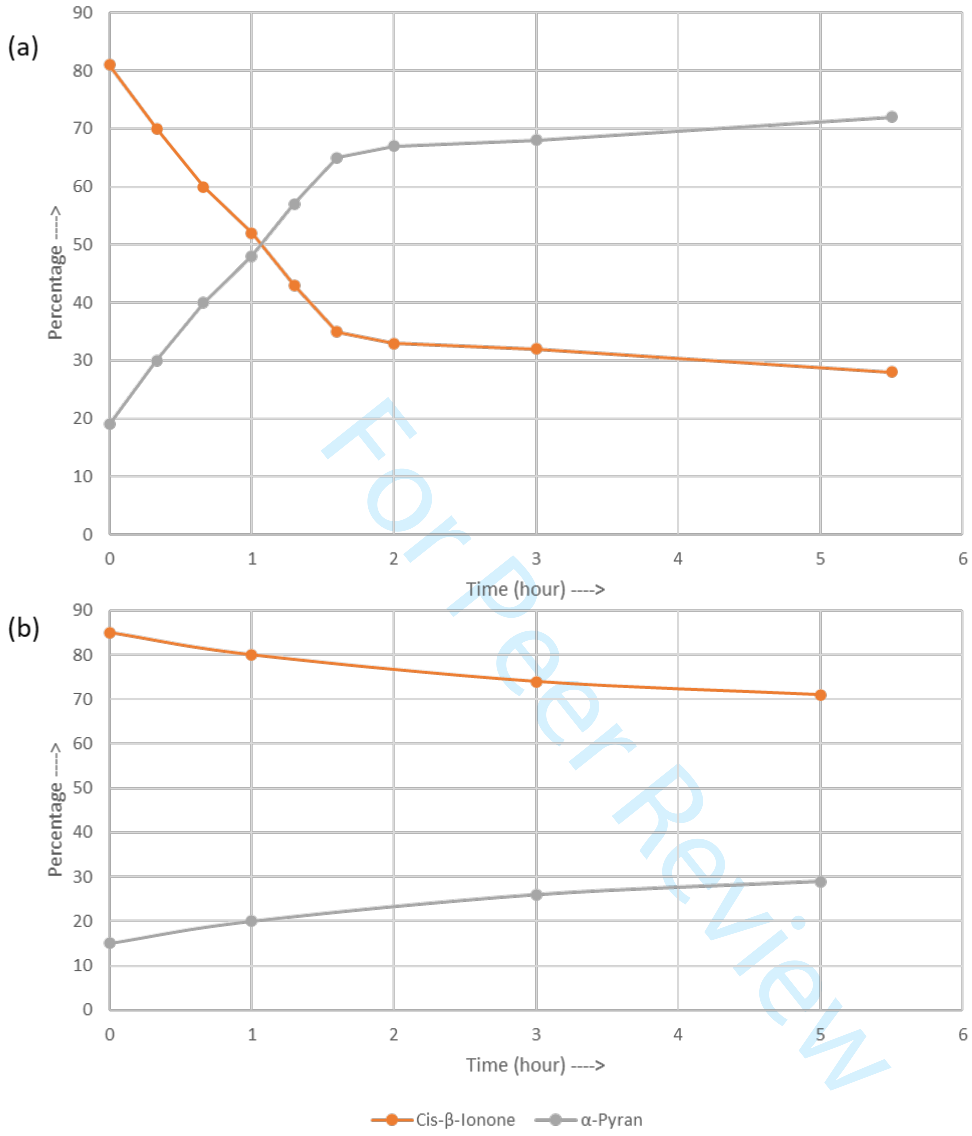
Cis-β-Ionone
α-Pyran

Figure 4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Time (hour) ---->
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70
60
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30
20
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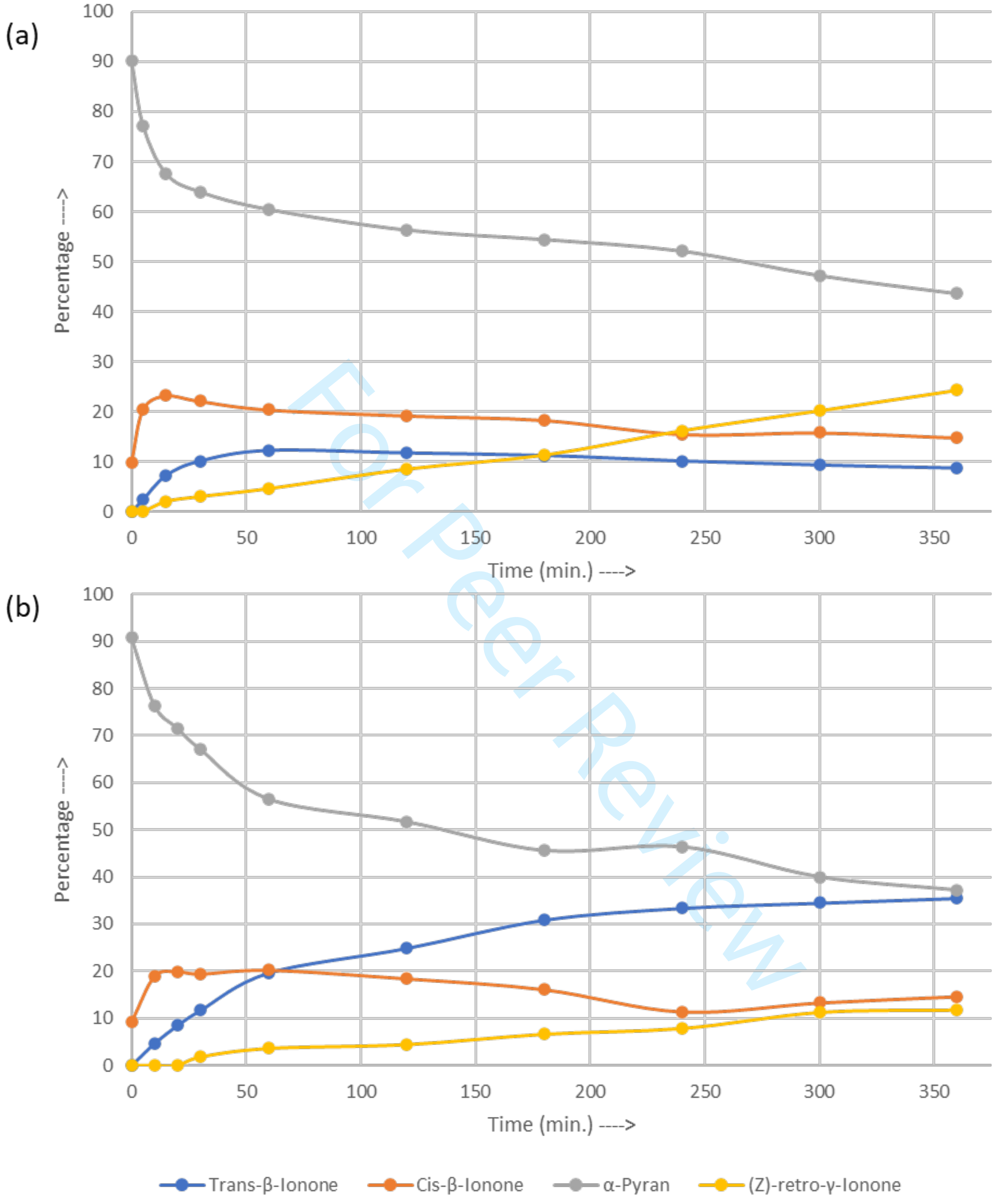
Time (hour) ---->
Cis-β-Ionone
α-Pyran

Figure 5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Trans-β-Ionone
Cis-β-Ionone
α-Pyran
(Z)-retro-γ-Ionone

Figure 6

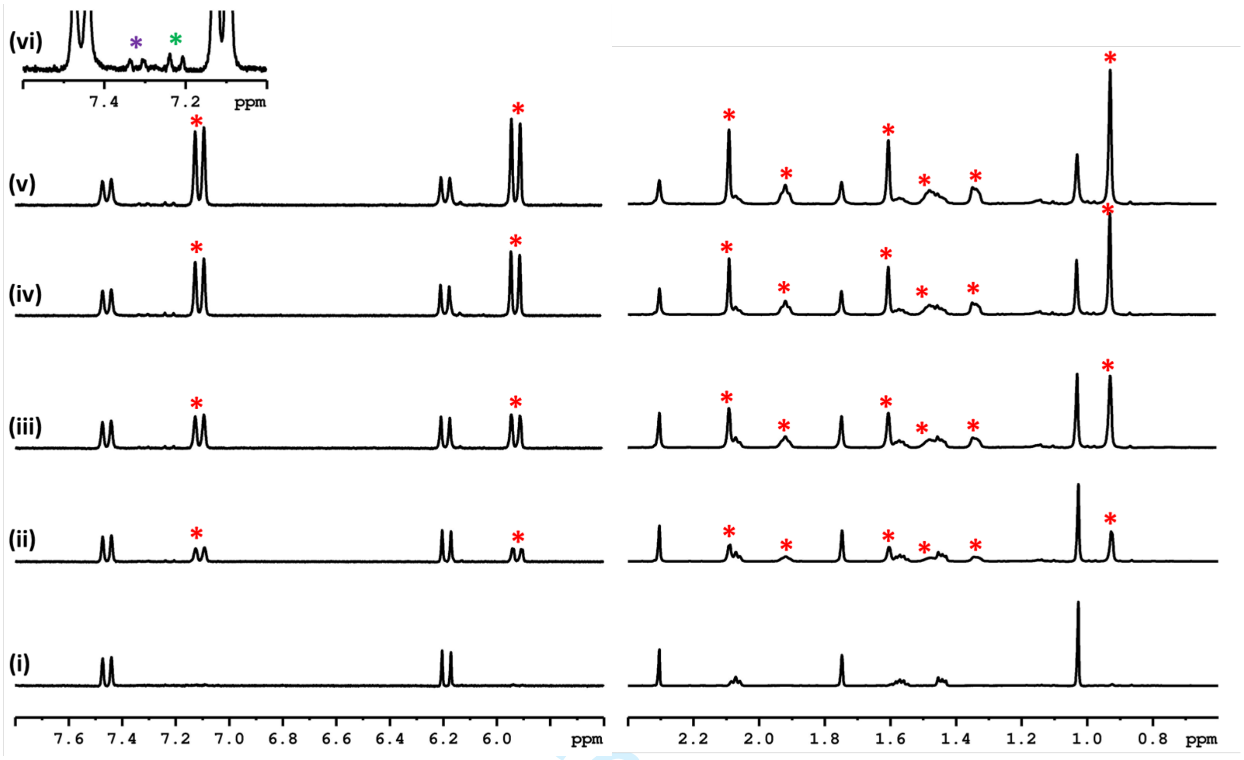
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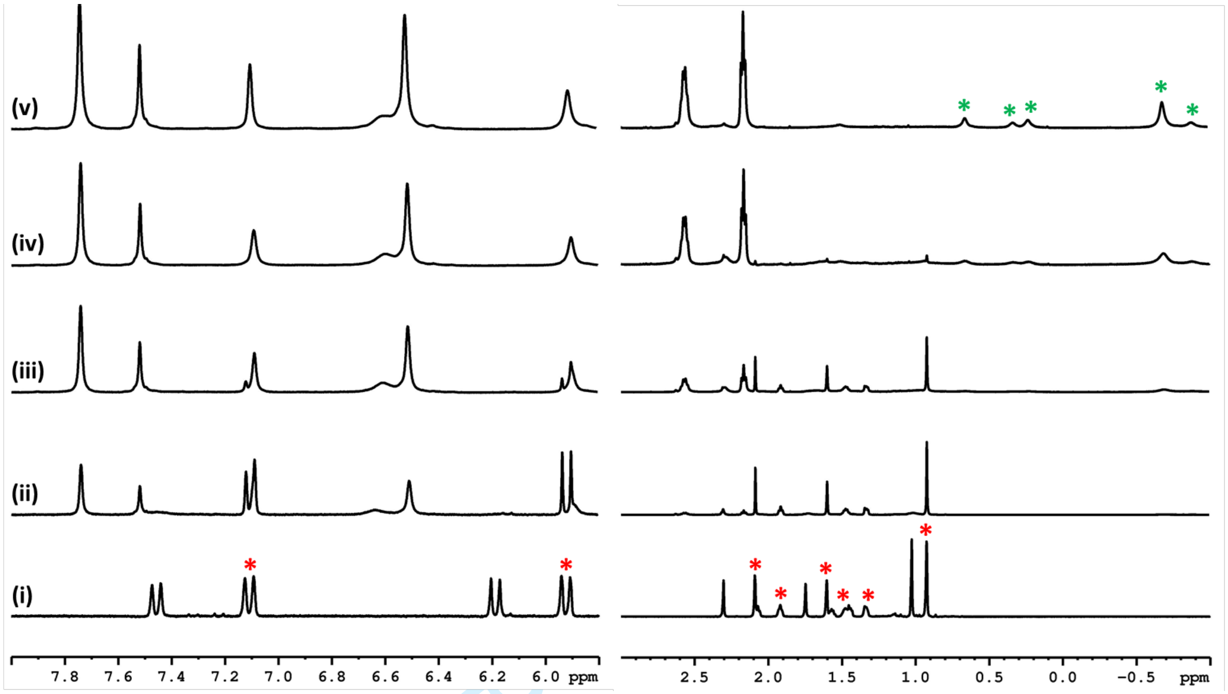
Figure 7



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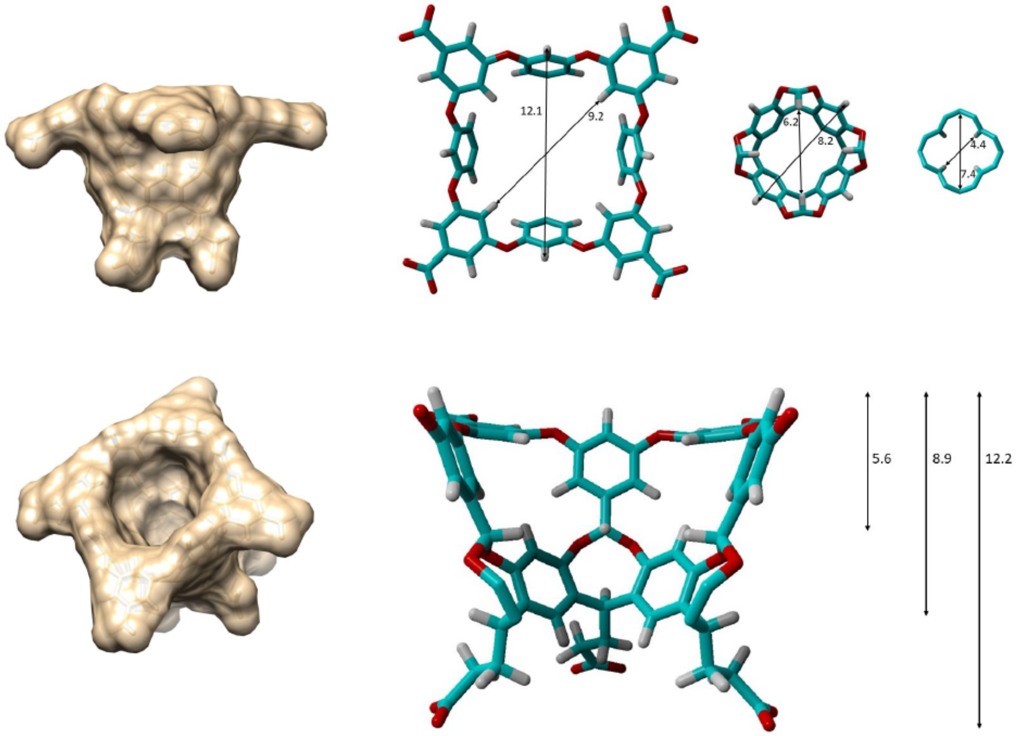
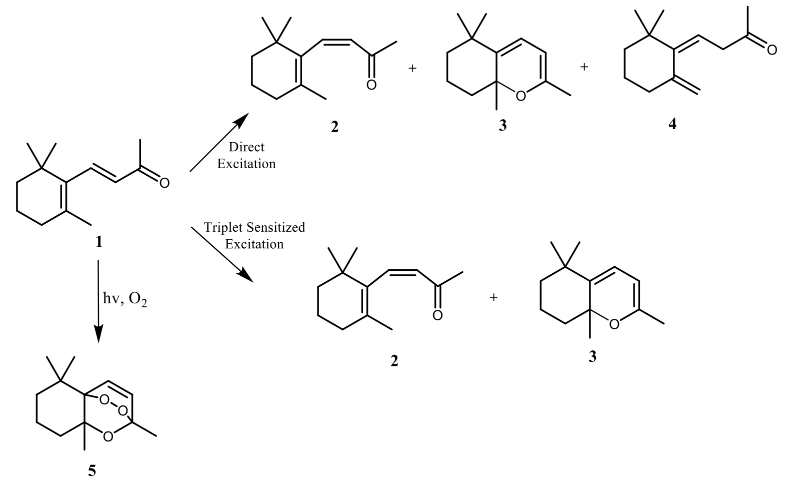


Figure 9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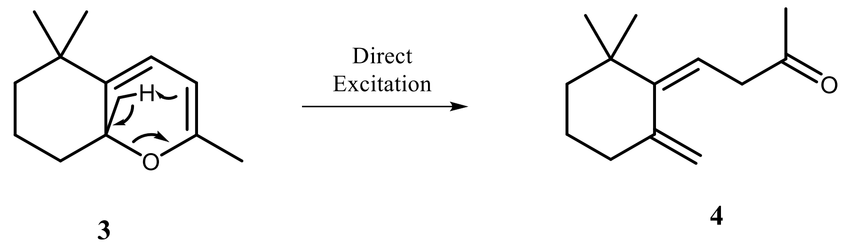
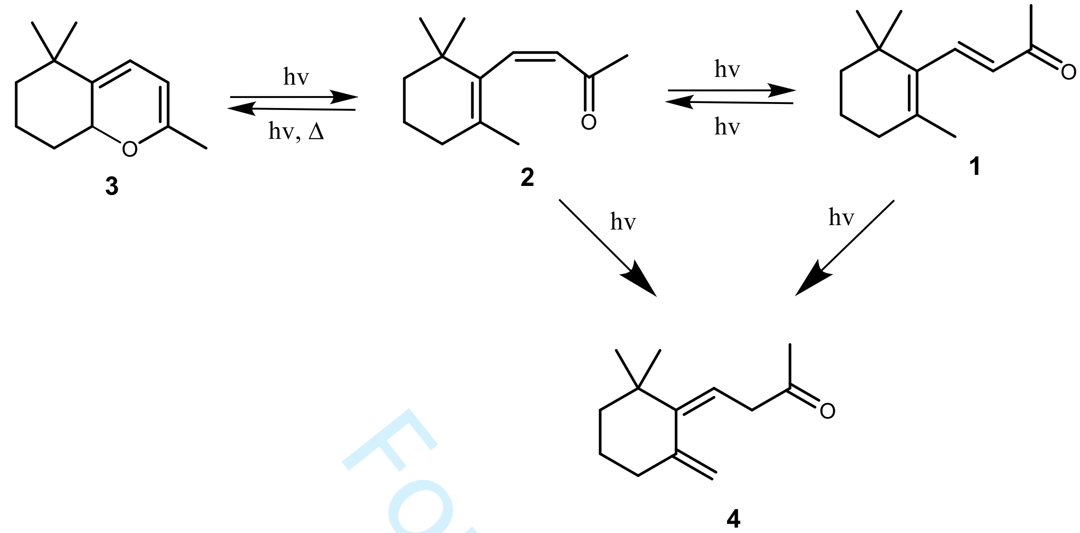
hν, O_2
5
O
O-O

Scheme 1



Scheme 2



Scheme 3