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Barrelene–semibullvalene rearrangement induced by visible light: synthesis of dicorannulenosemibullvalene dimethyl dicarboxylate

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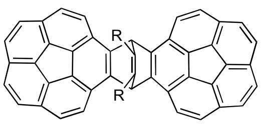
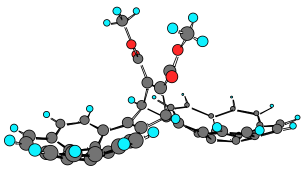
Abstract—A clean, quick conversion of biscorrannulenobarrelene dicarboxylate to the respective semibullvalene is observed upon irradiation of solutions of the former with a sun lamp. This represents the first reported example of such rearrangement induced by visible light. Hybrid density functional theory calculations predict the *exo–endo* conformer of the semibullvalene as the most stable, with the bis-*exo* and bis-*endo* conformers being higher in energy by ca. 1 and 4 kcal/mol, respectively.

As part of our continuing pursuit[1] of practical, condensed phase synthetic methods for the production of buckybowls (curved-surface polycyclic aromatic hydrocarbons related to buckminsterfullerene),[2] we recently reported the synthesis and crystal structure determination of a novel dimethylcarboxybarrelene **1** with two corannulene units attached to the sides of the central ring.[3]



1: R=COOMe



1a

From its three possible conformers the bis-*exo* **1a** was found to be the most stable by theory as well as experimentally in the solid state. In solution, however, all three conformers were detected by ^{1}H NMR at low temperatures, while fast bowl-to-bowl inversion of the flexible corannulene units at ambient temperature resulted in the appearance of a simple averaged spectrum with only five signals.[3]

However, we noticed recently that the spectrum changes with time when solutions of **1** are left standing on the bench, and since an inert atmosphere did not inhibit this process, we suspected that light was likely responsible for the observed changes. In fact, irradiation of solutions of **1** contained in NMR tubes with various solvents with an incandescent sun lamp results in a complete disappearance of the starting material in a matter of minutes. The only detectable product exhibits a more complicated NMR spectrum than the starting material, apparently the result of a loss of symmetry.

In contrast with the single signal for the two symmetry related carbomethoxy methyl groups in **1**, the new ^{1}H NMR spectrum indicated the presence of two carbomethoxy groups with singlets at 3.71 and 4.06 ppm. Similarly the singlet representing the two bridgehead protons in **1** disappears and is replaced by two new singlets (one proton each) at 5.12 and 6.12 ppm. In the ^{13}C NMR spectrum, the single absorption of the methyl groups ($COOCH_3$) in **1** is replaced by two signals at 52.7 and 53.5 ppm, and the single CH signal of the barrelene moiety is replaced by two CH signals at 48.4 and 51.9 ppm; two quaternary sp^3 carbon signals are also observed at 60.0 and 71.5 ppm. Comparison of the chemical shifts of the new species with published data of several dibenzosemibullvalenes[4] provides convincing evidence that the new species formed from **1** upon sun

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Keywords: Di-π-methane rearrangement; Photochemistry; Buckybowls.

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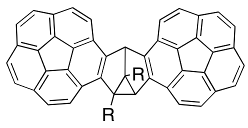
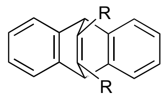
lamp irradiation is dicorannulenosemibullvalene dimethyl dicarboxylate **2**.[†]



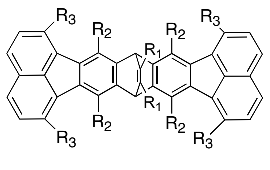
2: R = COOMe

The photochemical conversion of barrelenes to semibullvalenes has been studied since 1966;[5] it represents a sub-class of the di-π-methane rearrangement.[6] However, as far as we are aware, this rearrangement has only been observed upon UV irradiation. Thus the present example represents the first observation of a barrelene to semibullvalene conversion induced by visible light since the sun lamp applied here (Philips 250 W Reflector Infrared) produces radiation in the visible and infrared regions only. To assess just how facile this conversion may be with corannulenes as the aromatic segments, we investigated dibenzobarrelenes **3** and **4** under similar conditions. Not surprisingly, irradiation of solutions of dibenzobarrelene **3** with a sun lamp for several days did not lead to any photoisomerization.



3: R = COOMe

The larger model barrelene **4** was synthesized previously on the route to dicorannulenobarrelene **1**.[3] Despite the similar molecular size of **4** as compared to **1** we did not expect dramatic changes upon irradiation with visible light since we previously converted **4** to the corresponding dodecabromo derivative **5** in high yield by bromination with NBS/dibenzoyl peroxide in carbon tetrachloride with sun lamp irradiation, and no isomerization was observed under these conditions.[3] Indeed, brief irradiation of solutions of **4** does not cause any change in the NMR spectra. However, prolonged irradiation of **4** in deuterated chloroform with a sun lamp causes gradual decomposition. The product or products are likely polymeric since periodic monitoring by ^{1}H NMR shows a decrease in the intensity of signals without the appearance of a new set of signals. On the other hand, when a sample of **4** is carefully degassed and sealed under inert gas, decomposition upon sun lamp irradiation is significantly inhibited and there is slow conversion to a new species. While ^{1}H NMR suggests initial photochemical conversion of **4** into the respective semibullvalene,[‡] the process is very sluggish and does not lead to clean production of the semibullvalene. Rather prolonged (several days) irradiation produces a complicated mixture of products along with unreacted starting material.[§]



4: R_1 = COOMe
R_2=R_3=CH_3

5: R_1 = COOMe
R_2 = CH_2Br
R_3 = $CHBr_2$

The striking facility of the photoisomerization of **1** to **2**, as compared to model systems **3** and **4**, is likely due to better stabilization of the biradical intermediates postulated for di-π-methane rearrangements.[5–7] Apparently the corannulene moiety is more capable of delocalization of the unpaired electrons than the benzene ring in **3**, or the tetramethylfluoranthene fragment in **4**.

While we have not been successful in growing X-ray quality crystals to study the conformational preference of **2** in the solid, we have studied the relative stabilities of all three possible conformers **2a**–**c** at the same level of theory successfully applied[3] to the analogous system **1**.[¶] In contrast to **1**, which exhibits similar stabilities for all three conformers (all within ca. 1 kcal/mol),[3] the energy differences among the conformers of **2** are significantly larger. The *exo*–*endo* **2b** is predicted to be the most stable with the bis-*exo* **1a** and bis-*endo* **2c** having higher energies by ca. 1 kcal/mol, and more than 4 kcal/mol, respectively. The significantly higher energy of the bis-*endo* **2c** can be attributed to steric hindrance caused by the proximity of two hydrogen atoms of the two corannulene moieties (marked with asterisks in Fig. 1). In the optimized structure of **2c** this nonbonding

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[†] Off-white solid (from ethanol). Does not melt up to 400 °C, but decomposes gradually above 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) 8.52 (d, 1H, $J = 8.7$ Hz), 8.39 (d, 1H, $J = 8.7$ Hz), 8.02 (d, 1H, $J = 8.7$ Hz), 7.93 (d, 1H, $J = 8.7$ Hz), 7.88 (d, 1H, $J = 8.8$ Hz), 7.8–7.6 (m, 11H), 6.12 (s, 1H), 5.12 (s, 1H), 4.06 (s, 3H), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) 169.61, 169.37, 148.06, 146.99, 135.99, 135.80, 135.73, 135.66, 135.55, 135.51, 131.31, 131.15, 131.00, 130.72, 130.59, 130.47, 130.32, 129.41, 128.88, 128.79, 127.97, 127.93, 127.87, 127.80, 127.41, 127.36, 127.29, 127.24, 127.17, 127.09, 126.49, 125.91, 125.06, 124.99, 124.61, 71.69, 59.97, 53.51, 52.70, 51.91, 48.39. MS *m*/*z* (rel. intensity): 665 (56), 664 (100), 606 (32), 605 (66), 604 (28), 547 (29), 546 (54). HRMS (EI, 70 eV): calcd for $C_{48}H_{24}O_4$ 664.1669, found 664.1662.

[‡] Slow build up of new singlets at 3.79 and 3.96 ppm (presumably OCH_3) and 4.62 and 5.49 ppm (presumably CH) is consistent with the formation of semibullvalene.

[§] Secondary photoproducts resulting from prolonged UV irradiation of **3** and its derivatives have recently been reported.[4]

[¶] *Computational methods*: Hybrid Density Functional Theory methods were used at B3LYP level, that is, Becke's 3 parameter hybrid exchange functional[8] in combination with the Lee–Yang–Parr nonlocal correlation functional.[9] Geometry optimization was performed by employment of 6-31G(D) basis set for all oxygen atoms and for the eight carbon atoms of the central (semibullvalene) part of the molecule. 3-21G basis set was used for the remaining carbon atoms (we denote this basis sets combination as a GEN basis set). Additionally, single point energy calculations were performed at the B3LYP/6-311G* level. All calculations were carried out using the Gaussian98 suite of programs.[10]

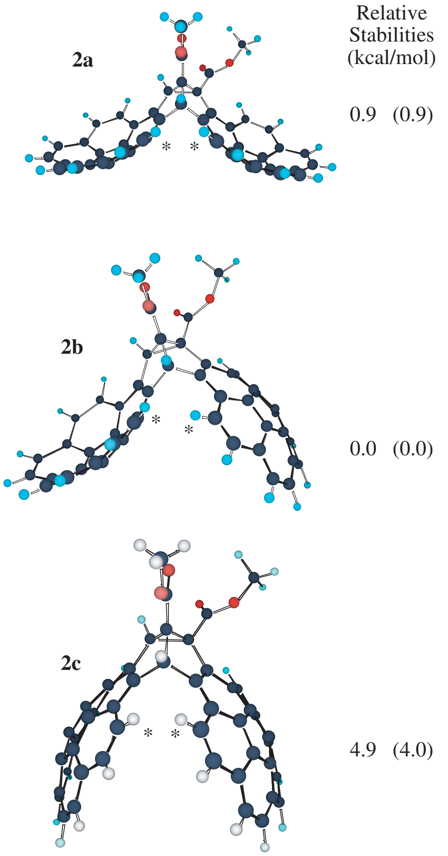
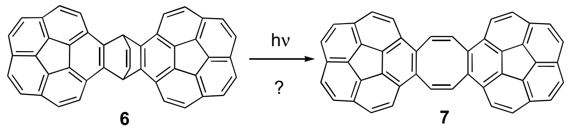


Figure 1. B3LYP/GEN optimized structures of possible conformers of **2** with their relative energies. The numbers in parentheses refer to the single point relative stabilities calculated at B3LYP/6-311G* level.

distance is only 1.94 Å, significantly lower than the sum of the van der Waals radii of two hydrogen atoms. On the other hand, the lower energy of the *endo–exo* **2b** as compared to di-*exo* **2a** cannot be explained by the same argument since the analogous H–H nonbonding distances are 2.28 and 2.61 Å, respectively.

As in **1**, fast bowl-to-bowl inversion of the flexible corannulene units results in the appearance of a NMR spectrum, which represents a weighted average of the possible conformers of **2** and any potential decoalescence of the spectrum is expected below ca. −50 °C. The calculated relative stabilities of **2a**–**c** suggest the NMR spectrum of **2** should not change much at low temperatures since **2b** may be the only conformer detectable. It is indeed the case—upon cooling of the solutions of **2** in acetone-d_6 from room temperature to −78 °C we observe broadening of the ^{1}H NMR bands with subsequent sharpening, but even at the lowest temperature attainable we are not able to detect more than one conformer. This is in contrast with **1**, which exhibited all three possible conformers at low temperatures.[2]

Irradiation of dibenzobarrelene itself is multiplicity-dependent. In the absence of photosensitizers, irradiation of dibenzobarrelene affords mainly dibenzocyclooctatetraene, presumably through a singlet pathway.[5a,11] However, irradiation in the presence of triplet-energy sensitizers, whether internal such as a carbonyl containing substituent, or external such as acetone as solvent, leads to semibullvalenes through a triplet process.[5] Thus, we are now pursuing the synthesis of barrelene **6**, which could presumably be photochemically converted to dicorannulenocyclooctatetraene **7**. The latter derivative will exhibit interesting conformational properties, and also has potential as a 'lithium sponge' considering the known high lithium affinity of both corannulene[12] and cyclooctatetraene.



In conclusion, we have observed a very facile photochemical conversion of barrelene **1** to semibullvalene **2** upon visible light irradiation. Comparison of the photochemical reactivity of **1** with model barrelenes **3** and **4** strongly emphasizes the role the corannulene moiety plays in stabilization of the crucial biradical intermediates in this di-π-methane rearrangement.[5–7] The *exo*–*endo* conformer **2b** is predicted to be most stable by HDFT calculations and it is presumably observed as a sole conformer as evidenced by ^{1}H NMR experiment at −78 °C in acetone-d_6 solutions.

Acknowledgements

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