DFT calculations of pentalenoquinones: towards the interception of 2-bromopentalene-1,5-dione

Taner Atalar,[a] Fatih Algı,[a,b] and Metin Balci[a]*

[a]Department of Chemistry, Middle East Technical University, 06531, Ankara, Turkey
[b]Laboratory of Organic Materials, Department of Chemistry, Çanakkale Onsekiz Mart University, 17100, Çanakkale, Turkey
E-mail: mbalci@metu.edu.tr

This paper is dedicated to Professor Udo H. Brinker on the occasion of his 65th birthday

Abstract

To reveal the stability and the aromatic character of pentalenoquinones (PQs) **1-4** and the corresponding bromo derivatives (Br-PQs) **6-9**, DFT calculations (B3LYP/6-311+G(d,p)) concerning the geometry optimization, total energy and nucleus independent chemical shift (NICS) values were performed. It was found that all of the compounds have planar geometry. As the energy difference between HOMO-LUMO energy levels ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) and total energies were considered for the pentalene family, the stability order was found to be **1** > **2** > **3** > **4** for PQs, and **6** > **7** > **8** > **9** for Br-PQs. Furthermore 2-bromopentalene-1,5-dione (**6**) in solution was investigated and noted that it was too reactive to be isolated or even trapped.

Keywords: Pentalene, pentalenoquinones, DFT calculations

Introduction

Pentalenoquinones (PQs) **1-4**, quinone derivatives of pentalene (**5**), may be defined as fully unsaturated derivatives of various isomeric bicyclo[3.3.0]octanediones and have fascinated scientists due to their extraordinary physical and chemical properties (Figure 1). For example, Delamere *et al.* have reported on the geometries, bond orders, chemical hardness, the NICS values and homodesmoric ring-opening reactions.[1] Recently, Yavari and *co-workers*[2] reported the structural optimization of PQs with semi-empirical and *ab initio* calculations, providing a picture of geometries of PQs from both structural and energetic points of view; and 1,5-PQ, **1**, was calculated to be the most stable isomer, albeit elusive.
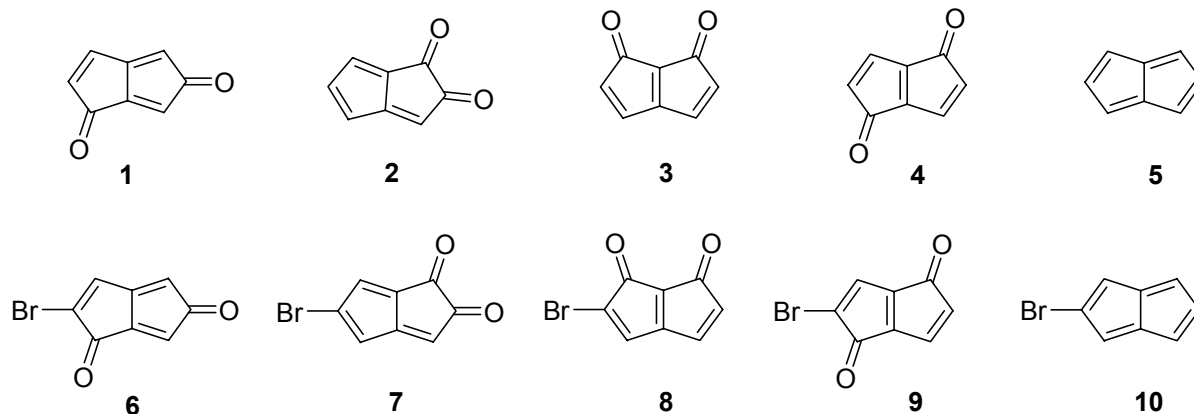
Figure 1

Although the chemistry of PQs, such as **1**, has been the subject of some theoretical studies, the extent of our present understanding regarding the stability, Diels-Alder and the (non)aromatic character of **1** is meager due to the lack of an extensive theoretical study as well as experimental evidence which demonstrates the existence of free **1**.[3] Herein we wish to report the results of our research in this field concerning DFT calculations geometry optimization, total energy and nucleus independent chemical shift (NICS) values[4] for the pentalene family, **1-10**. Furthermore, the fate of 2-bromopentalene-1,5-dione (**6**) in solution was investigated.

Results and Discussion

Theoretical calculations
We first ran DFT calculations for compounds **1-5**. Geometry optimizations were performed at the level of B3LYP/6-311+G(d,p)[5-7] to reveal at least a local minimum on the potential energy surface for each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Figure 2 shows the optimized structures for compounds **1-5** and bond lengths in Å, respectively.
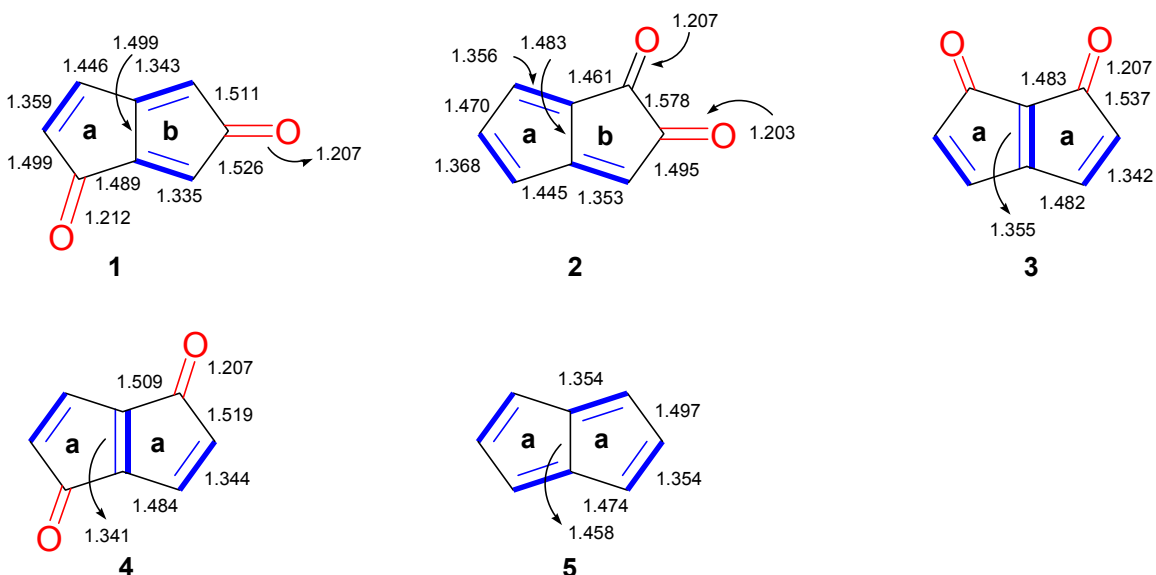
Figure 2. The geometry optimized structures of compounds **1-5** and the bond lengths in Å (a and b indicate the ring for NICS calculations).

Table 1. HOMO and LUMO energies (ε in eV), NICS values (in ppm), point groups and dipole moments (in Debye) (B3LYP/6-311+G(d,p)) for the geometry optimized structures of compounds **1-10**

	HOMO	LUMO	Δε	a	b	Point group	Dipole moment
				NICS (0)			
1	-7.386	-3.521	3.865	2.9	4.6	C_S	4.032
2	-6.903	-3.729	3.174	-0.4	6.9	C_S	6.509
3	-6.932	-4.101	2.831	6.5		C_{2v}	6.198
4	-6.719	-4.170	2.549	12.6		C_{2h}	0.000
5	-5.515	-2.940	2.575	24.3		C_{2h}	0.000
6	-7.374	-3.625	3.749	2.5	3.2	C_S	3.429
7	-7.059	-3.906	3.153	-2.7	6.9	C_S	5.557
8	-6.886	-4.257	2.629	8.5	6.2	C_S	6.120
9	-6.657	-4.361	2.296	11.2	9.2	C_S	1.018
10	-5.693	-3.188	2.505	21.1	23.1	C_S	1.741

For the optimized structures, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies (ε in eV), dipole moments (in Debye) and point groups were listed in Table 1. As the difference between HOMO-LUMO energy levels (Δε = $\varepsilon_{LUMO} - \varepsilon_{HOMO}$) was considered, the order was found to be **1** > **2** > **3** > **4** for PQs.

In order to evaluate what effect a bromine atom would have on the energy profile of compounds **1-5**, we performed DFT calculations at the same level for the corresponding bromo derivatives **6-10** (Fig. 3.). It was found that the presence of a bromine atom in the structure

causes elongation or contraction of certain bonds (for example compare **1** and **6**). When the difference between HOMO and LUMO energy levels ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) was considered, the order was found to be **6** > **7** > **8** > **9** for bromo-PQs. Furthermore, we noticed that the insertion of bromine atom decreased the energy gap ($\Delta\varepsilon$) between HOMO and LUMO.
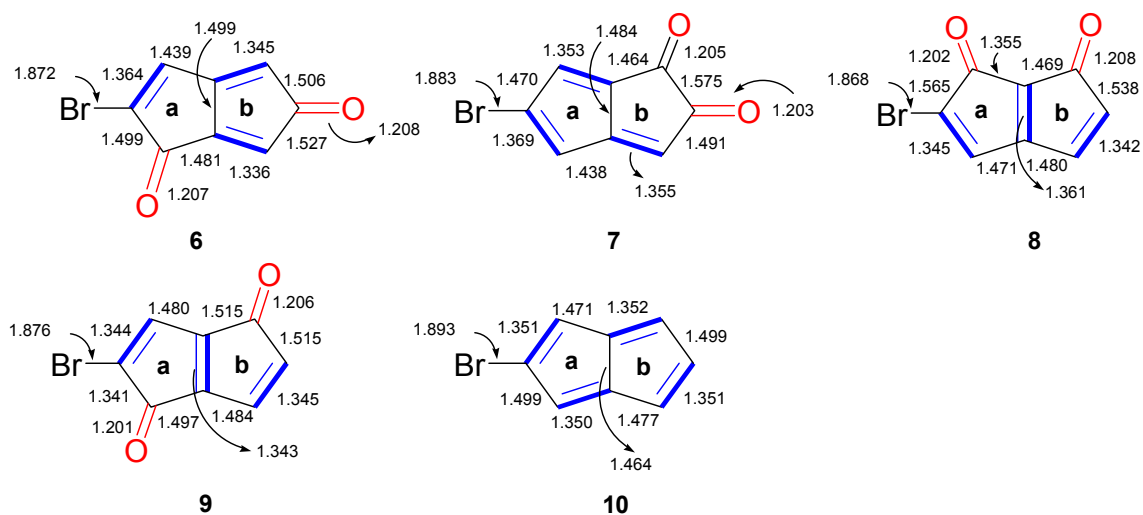

Figure 3. The geometry optimized structures of compounds **6-10** and the bond lengths in Å (a and b indicate the ring for NICS calculations).

It is well established that Nucleus Independent Chemical Shift (NICS) is an indication of aromatic and/or anti-aromatic character for a given system.[4] To get insight into the aromatic character of each member of the pentalene family, NICS values (in ppm) were calculated at B3LYP/6-311 G (d,p) level of theory based on the B3LYP/6-311 + G(d,p) optimized structures. NICS (0) calculations showed that there is no definite indication of aromatic and/or anti-aromatic character for PQs and Br-PQs. This result is consistent with previous findings in the literature.[1] However, it is worth noting that the bromine atom insertion generally decreased the NICS (0) values especially in the case of ring **a**. For example, on the one hand for pentalene, the NICS (0) value was decreased from 24.3 ppm to 21.1 ppm (compare **5** and **10** in Table 1), while on the other hand, for **3** and its bromo derivative **8**, the NICS (0) value was increased from 6.5 ppm to 8.5 ppm (Table 1).

Table 2. Calculated energies of compounds **1-10**

	Total Energy (a.u)	ZPE (kJ/mol)	Enthalpy (kJ/mol)	Relative Enthalpy[a] (kJ/mol)
1	-457.758800	251.712	-1201573	0[b]
2	-457.758451	252.159	-1201572	1[b]
3	-457.735980	249.971	-1201515	58[b]
4	-457.733803	249.553	-1201509	64[b]
5	-308.447479	287.935	-809524	-
6	-3031.299190	225.568	-7958431	0[c]
7	-3031.299150	225.664	-7958430	1[c]
8	-3031.276950	224.258	-7958373	58[c]
9	-3031.272450	223.495	-7958362	69[c]
10	-2881.989330	262.129	-7566385	-

[a] Relative enthalpies were calculated from the enthalphy values obtained at 25°C and 1 atm. [b] These values were calculated relative to the most stable isomer **1**. [c] These values were calculated relative to the most stable isomer **6**.

To sum up the theoretical results, the lowest symmetry point group was found to be C_s for the molecules and all of them have planar geometry. As the difference between HOMO-LUMO energy levels ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) was considered for the pentalene family **1-10**, the order was found to be **1** > **6** > **2** > **7** > **3** > **8** > **5** > **4** > **10** > **9**. Generally, the high energy gap value resulting from the relatively high energy of LUMO and low energy of HOMO indicates that neither losing nor capturing an electron will occur easily and, thus the compound is expected to be stable. Table 2 indicates some calculated energies of species at the B3LYP/6-311+G(d,p) level of theory. All the results showed that the stability order is **1** > **2** > **3** > **4** for PQs and **6** > **7** > **8** > **9** for Br-PQs. The calculated energy difference between the most favorable and unfavorable species is 64 and 69 kJ/mol for PQs and Br-PQs, respectively. In terms of total energy and enthalpy values, finding the stability order is similar to the stability order obtained in the case of frontier molecular orbital energy gaps. These theoretical results encouraged us to investigate the fate of **6** in solution, since it looks quite feasible among the others.
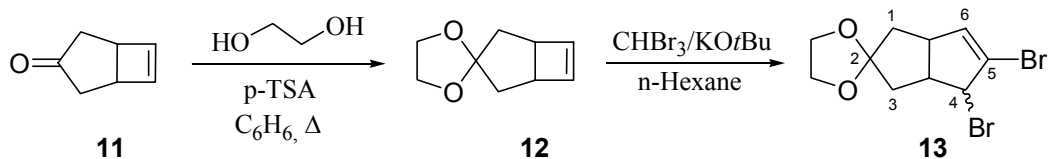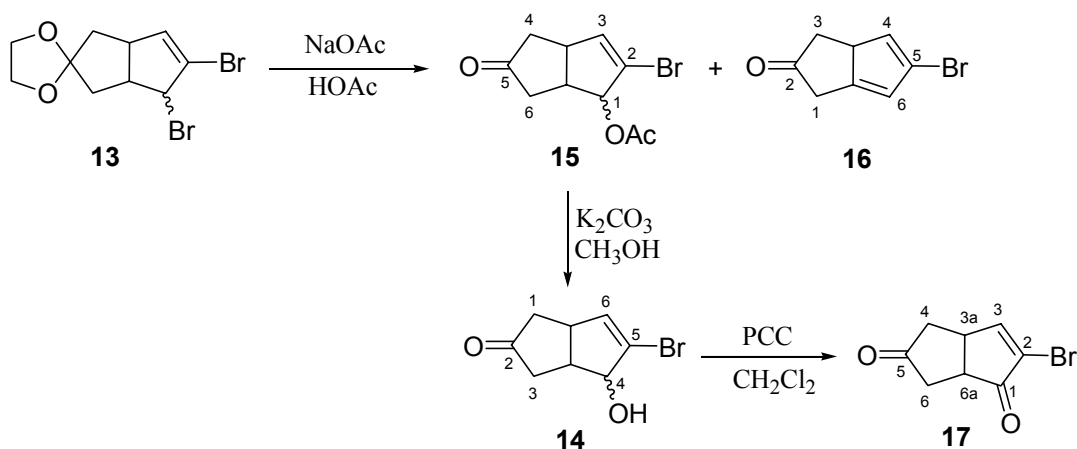

Scheme 1

In order to obtain the desired skeleton, we started with the known ketone **11**.[8] Dibromo carbene addition to the double bond after protection of the carbonyl moiety with ethylene glycol in the presence of acid, provided **13** (Scheme 1) whose structure was elucidated on the basis of NMR spectral data. Careful inspection of the ^{1}H-NMR spectrum indicated the presence of two isomers (*exo-* and *endo-*) in a ratio of 3:1, respectively. The ^{1}H-NMR spectrum of *exo*-**13** shows five sets of signals. The olefinic proton (H-6) appear as doublet at 5.93 ppm ($J = 2.1$ Hz) whereas the proton H-4 appears as a broad singlet at 4.62 ppm. The protons of the ring junction (H-3a and H-6a) give rise to multiplets between 3.50-3.00 ppm. A ten-line (see below) ^{13}C-NMR spectrum is also in agreement with the structure.
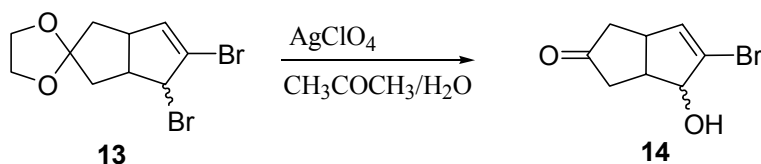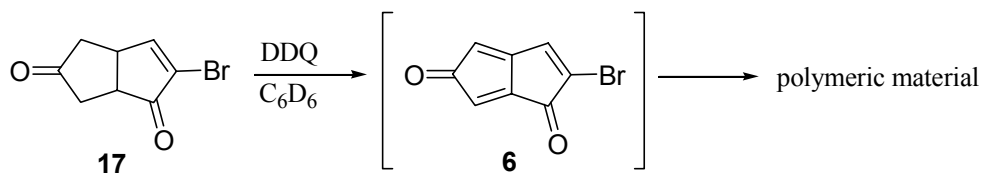

Scheme 2

Interestingly, when compound **13** was treated with AgClO$_4$ in moist acetone, a mixture of hydroxy ketone **14** was the only isolated product and in 25% yield (Scheme 2). In an attempt to increase the yield of hydroxy ketone **14**, we found that the reaction of **13** with NaOAc in HOAc provides compound **15** along with a minor product identified as **16** (Scheme 3). The ^{1}H-NMR spectrum of **16** indicated two olefinic protons resonate at 6.83 ppm (bs) and 5.79 (d, $J = 1.8$ Hz). The proton at the ring junction appears at 3.55 ppm as a triplet ($J = 5.6$ Hz), whereas the methylenic protons appear as two different AB systems between 3.00-2.00 ppm. The ^{13}C-NMR spectrum with eight signals was consistent with the assigned structure. Compound **16** arises from the competing elimination of AcOH under the given conditions. Formation of **16** could be suppressed by lowering the temperature.

Scheme 3

Treatment of **15** with K$_2$CO$_3$ in CH$_3$OH as the solvent followed by PCC oxidation of alcohol **14** in CH$_2$Cl$_2$, furnished the dione **17** in high yield (Scheme 3). In the ^{1}H-NMR spectrum of **17**, the proton H-3 appears at 7.68 ppm (d, $J = 3.0$ Hz) as expected. However, the protons H-3a and H-6a resonate at 3.58 (m) and 3.17 (ddd, $J = 11.9$, 6.6 and 5.0 Hz). On the other hand, the methylenic protons give rise to two sets of AB systems between 2.80-2.00 ppm.[9]

Our initial exploratory efforts directed towards the dehydrogenation of **17** involved the use of selenoxide elimination.[10] Disappointingly, the reaction did not proceed with **17** being recovered, unaltered.

Scheme 4

Dehydrogenation of **17** with dicyanodichloro-*p*-benzoquinone (DDQ)[11] in benzene for 12 h at ambient temperature indicated that ketone **17** was consumed but gave an insoluble polymeric material. Repeating the reaction either in the presence of furan or in benzene-*d$_6$* under similar conditions gave the same results. This suggests, that **6** probably undergoes sequential intermolecular cycloaddition as soon as it is formed due to its high reactivity.

Conclusions

In summary, DFT calculations (B3LYP/6-311+G(d,p)) concerning the geometry optimization, total energy and nucleus independent chemical shift (NICS) values were performed in order to reveal the stability and aromatic character of PQs **1-4** and Br-PQs **6-9**. It was found that all of them have planar geometry and if the difference between HOMO-LUMO energy levels ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) and total energies were considered, the stability order was found to be **1 > 2 > 3 > 4** for PQs, and **6 > 7 > 8 > 9** for Br-PQs. Furthermore, despite the quantum chemically indicated stability of PQ **6** when compared to other isomers, experimental results suggests that it is still too reactive to be isolated or even trapped in solution.

Experimental Section

General Procedures. Supplementary data concerning the details of the DFT calculations can be found in the online version via the internet. Geometry optimizations were performed at the level of B3LYP/6-311+G(d,p). The nucleus independent chemical shift (NICS) was used as a

descriptor of aromaticity from the magnetic point of view. The index is defined as the negative value of the absolute magnetic shielding computed at ring centers or another interesting point of the system. In this study, NICS values were computed with GIAO B3LYP/6-311G (d,p) // B3LYP/6-311+G(d,p). NICS (0) was calculated at the geometrical center of the ring. For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All the calculations for the geometry optimizations and energies were performed using Gaussian 98 program package and Spartan 06 package programme.

Infrared spectra were recorded on a Mattson model 1000 FT-IR spectrometer. ^{1}H- and ^{13}C- NMR spectra were recorded on 400 and 100 MHz spectrometers (Brucker/Avance), respectively. Column chromatography was performed on silica gel (60-200 mesh) from Merck Company. TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminum plates. All the solvent purification was done as stated in the literature.[12]

Spiro[bicyclo[3.2.0]hept-6-ene-3,2'-[1,3]dioxolane] (12). Bicyclo[3.2.0]hept-6-en-3-one **11**[13] (5 g, 0.046 mol), ethane-1,2-diol (5.7 g, 0.09 mol), catalytic amount of *p*-toluene sulphonic acid and anhydrous benzene (50 mL) were placed in a round-bottomed flask fitted with a Dean-Stark water separator and a reflux condenser. The reaction mixture was heated until no more, water collected. The reaction was also monitored by TLC. The mixture was cooled, the ethylene glycol layer was separated, and the benzene layer was washed succesively with saturated sodium bicarbonate solution and brine, dried over $MgSO_4$. Removal of solvent gave **12** as a colorless oily liquid (5.6 g, 0.037 mol) in a yield of 80%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.0 (s, 2H), 3.7-3.9 (AA'BB' system, 4H), 3.2 (t, J = 3.2 Hz, 2H), 1.8 (bs, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.9, 119.5, 65.1, 63.6, 46.1, 38.8. IR ($CHCl_3$, cm^{-1}) 3035, 2933, 1741, 1425, 1334, 1273, 1177, 1123, 1075, 1051, 1013, 762, 555. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.90; H, 7.90.

4',5'-Dibromo-3',3a',4',6a'-tetrahydro-1'H-spiro[1,3-dioxolane-2,2'-pentalene] (13). A solution of 9.17 g (36 mmol) $CHBr_3$ in *n*-hexane (20 mL) was dropwise added to a mixture of 5 g (33mmol) ketal **12** and 4.41 g (39 mmol) KOBu-t in *n*-hexane (80 mL), with magnetically stirring at 0°C over a period of 6 hours. The organic layer was washed first with water and brine, dried over $MgSO_4$. The residue was crystallized from *n*-hexane to give a mixture of *exo*- and *endo*-**13** (3.95 g, 26 mmol, 78%) in a ratio of 3:1, respectively. NMR data of each isomer was extracted from the NMR spectrum of a mixture.

Exo-**13:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.93 (d, J = 2.1 Hz, 1H), 4.62 (bs, 1H), 3.79 (bs, 4H), 3.36-3.28 (m, 1H), 3.18 (q, J = 8.4 Hz, 1H), 2.06-1.94 (m, 2H), 1.64-1.55 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.5, 122.7, 117.4, 65.2, 64.5, 64.0, 50.9, 46.3, 41.3, 39.1. IR ($CHCl_3$,

cm^{-1}): 2885, 1742, 1602, 1430, 1334, 11092, 1089, 1016, 947, 795, 723, 436. Anal. Calcd for C$_{10}$H$_{12}$Br$_2$O$_2$ (*endo- exo*-mixture) : C, 37.07; H, 3.73; Br, 49.32. Found: C, 36.95; H, 3.65.

Endo-**13:** ^{1}H-NMR (400 MHz, CDCl$_3$) δ 5.77 (d, J = 2.1 Hz, 1H), 4.49 (bs, 1H), 3.79 (bs, 4H), 3.36-3.28 (m, 1H), 3.00 (q, J = 7.5 Hz, 1H), 2.06-1.94 (m, 2H), 1.64-1.55 (m, 2H).

Reaction of 5-Bromo-1,3a,4,6a-tetrahydro-4-hydroxypentalen-2(1H)-one (14) with AgClO$_4$. To a magnetically stirring solution of 1.41 g (6.79 mmol) AgClO$_4$ in 40 ml of acetone and 30 mL of distilled water was dropwise added a solution of 2 g (6.17 mmol) of **13** in 30 mL of acetone at room temperature. The mixture was further stirred for 2 hours and precipitated AgBr was filtered off. The solution was extracted with ether (3x100 mL), and combined organic phases were washed with brine, dried over MgSO$_4$. After removal of solvent with a rotary evaporator, the alcohol **14** (0.34 g, 1.5 mmol) was obtained in a yield of 25%.

Acetylation of 13. 5 g (15.4 mmol) of **13** and 2.3 g. (16.9 mmol) of NaOAc were dissolved in 15 mL of glacial acetic acid. The mixture was heated up to reflux for 14 hours. Then the mixture was washed with saturated NaHCO$_3$, and extracted with ether (3x30 mL), dried over MgSO$_4$, the solvent was evaporated. Column chromatography on silica gel with 3% ethyl acetate/*n*-hexane as eluent gave compound **15** (3.12 g, 12 mmol, 78%), and **16** as a single isomer (0.51 g, 2.5 mmol, 16%).

2-Bromo-5-oxo-1,3a,4,5,6,6a-hexahydro-pentalen-1-yl-acetate (15). Colorless oily liquid, ^{1}H-NMR (400 MHz, CDCl$_3$) δ 6.10 (d, J = 1.9 Hz, 1H), 5.33 (bs, 1H), 3.60 (m, 1H), 3.33-3.39 (m, 1H), 2.82 (m, A part of AB system, 1H), 2.61 (dd, B part of AB system, J = 10.8-19.3 Hz, 1H), 2.42 (dd, A part of AB system, J = 10.1-19.0 Hz, 1H), 2.18 (m, B part of AB system), 2.06 (s, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ 216.6, 170.9, 141.4, 122.1, 87.3, 44.9, 42.9, 42.0, 38.2, 21.3. IR (CHCl$_3$, cm^{-1}): 2979, 2958, 2916, 2867, 2846, 2063, 1749, 1630, 1455, 1399, 1371, 1231, 1161, 1057, 1022, 812, 735, 651. Anal. Calcd for C$_{10}$H$_{11}$BrO$_3$: C, 46.36; H, 4.28; Br, 30.84. Found: C, 46.27; H, 4.22.

3-Bromo-3,3a,-dihydro-1H-pentalen-2-one (16). Colorless liquid, ^{1}H-NMR (400 MHz, CDCl$_3$) δ 6.83 (bs, 1H), 5.79 (d, J = 1.8 Hz, 1H), 3.55 (t, J = 5.6 Hz, 1H), 3.00 (dd, A part of AB system, J= 7.3-16.8 Hz, 1H), 2.68 (m, B part of first AB system and A part of the second AB system, 2H), 2.34 (dd, B part of the second AB system, J = 5.1-17.1 Hz, 1H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ 208.5, 154.2, 142.2, 129.8, 118.0, 47.7, 45.1, 41.9. IR (CHCl$_3$, cm^{-1}): 2968, 1734, 1604, 1584, 1266, 1108, 899, 812, 695. Anal. Calcd for C$_8$H$_7$BrO: C, 48.27; H, 3.54. Found: C, 48.20; H, 3.47.

5-Bromo-1,3a,4,6a-tetrahydro-4-hydroxypentalen-2(1H)-one (14) via hydrolysis 1.07 g (7.72 mmol) unhydrous K$_2$CO$_3$ and 2 g (7.72 mmol) of **15** were dissolved in 30 mL of CH$_3$OH at room temperature. The reaction was monitored by TLC. After 1 hour, mixture was extracted with ethyl acetate (3x30 mL), combined organic layers were dried over MgSO$_4$, and the solvent was removed to give alcohol **14** (1.50 g, 7.0 mmol,) in a yield of 90%. ^{1}H-NMR (400 MHz, CDCl$_3$) δ 6.07 (d, J = 1.7 Hz, 1H), 6.05 (d, J = 2.1 Hz, 1H), 4.77 (d, J = 7.3 Hz, 1H), 4.47 (bs, 1H), 3.60 (m, 1H), 3.30 (m, 1H), 3.20 (m, 1H), 3.00 (m, 1H), 2.70-2.10 (m, 4H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ 218.1, 135.9, 126.4, 85.9, 45.9, 44.0, 43.1, 37.3. IR (CHCl$_3$, cm^{-1}): 3399, 2921, 2847,

1732, 1613, 1398, 1314, 1165, 1058, 822. Anal. Calcd for $C_8H_9BrO_2$: C, 44.27; H, 4.18. Found: C, 44.21; H, 4.02.

2-Bromo-3a,4,6,6a-tetrahydro-pentalene-1,5-dione (17). To a magnetically stirring solution of 2.7 g (12.6 mmol) PCC in 30 mL CH_2Cl_2 at 0 °C, was dropwise added a solution of 2.50 g (11.5 mmol) of alcohol **14** in 20 mL CH_2Cl_2. After stirring for additional 5 hours at RT, the reaction mixture was filtered off through a short silica gel column by eluting with CH_2Cl_2 to give **17** as a colorless liquid (2.13 g, 10.5 mmol, 92%). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.68 (d, J = 3.0 Hz, H-6), 3.62-3.56 (m, H-3a), 3.17 (ddd, J = 11.9, 6.6 and 5.0 Hz, H-6a), 2.80 (m, A parts of the two AB systems overlapped, 2H), 2.40 (dd, B part of the AB system, J = 19.5 and 3.8 Hz, 1H), 2.15 (dd, B part of the AB system, J = 18.8 and 4.2 Hz, 1H). ^{13}C-NMR (100 MHz, CDCl$_3$) δ 212.7, 201.1, 162.8, 127.1, 44.1, 41.1 (2C), 40.2. IR (CHCl$_3$, cm[-1]): 1738, 1274, 1259, 909, 762, 747. Anal. Calcd for $C_8H_7BrO_2$: C, 44.68; H, 3.28; Br, 37.16. Found: C, 44.45; H, 3.20.

Treatment of 17 with DDQ. To a magnetically stirring solution of solution of **17** (200 mg, 1 mmol) in 5 mL benzene was dropwise added a solution of DDQ (250 mg, 1.1 mmol) in 5 mL benzene. After total consumption of starting ketone (12 h, TLC), the solvent was removed under reduced pressure to give the polymeric compound. The same procedure was also repeated both in the presence of furan and C_6D_6 to give the same result.

Acknowledgements

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