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Contraction of π -Conjugated Rings upon Oxidation from Cyclooctatetraene to Benzene via Tropylium Cation

Akira Tamoto,^[a] Naoki Aratani*^[a] and Hiroko Yamada*^[a]

Dedication

Abstract: We have serendipitously discovered the unique transformation of a cyclooctatetraene derivative **1** for the first time in 60 years, to a cycloheptatriene spirolactone **3** upon oxidation. The product **3** could be reversibly interconverted to the aromatic tropylium cation **3H**⁺ by acid/base accompanying drastic spectral changes. The resultant cycloheptatriene could be further converted to benzene upon oxidation. We could characterize all the key structures by X-ray analysis. Eventually, the π -conjugated ring size shrinks from 8 to 7, then finally 6 upon oxidation, directing to the stronger aromatization.

Introduction

60 Years ago, Ganellin and Pettit discovered the transformation of cyclooctatetraene (COT) to the tropylium cation upon the oxidation.^[1] Although whole reaction mechanism and intermediates were unclear especially for the structure of acid at that time, they considered that this reaction includes pinacol-pinacolone rearrangement and 2e⁻ transfer processes (Scheme 1). Since then, this chemistry has been left untouched to date except for a few related reports.^[2]



Scheme 1. Ganellin and Pettit's proposal for the reaction of cyclooctatetraene upon oxidation.

From the point of view of aromatic characteristics, this transformation has implications of their structural stability. Oxidation of 8π COT that is non-planar non-aromatic compound results in the formation of 6π (formally stable) aromatic tropylium cation^[3] accompanying with carbon-skeleton rearrangement. On the other hand, Olah et al. reported direct $2e^-$ oxidation of methylated COT to 6π aromatic COT dication at low temperature.^[4]

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Recently, another unique skeletal rearrangements of COT derivatives under oxidative conditions were independently reported by Tobe^[5] and Kawase.^[6] Tobe's group reported the skeletal rearrangements of a twisted polycyclic aromatic hydrocarbon (PAH) to afford a product with a seven-membered ring and then tetrabenzocoronene with all six membered rings.^[5] The rearrangement was interpreted in terms of the acid-catalyzed isomerization of 9,9'-bifluorenylidene into dibenzo[*g*,*p*]chrysene moieties. Scott and Kawase reported that the bicyclo[6.3.0]undecapentaenyl cation afforded azulene upon oxidation followed by decarbonylation.^[6]

Tetra[(1.8)-naphthylene]-1,3,5,7-cyclooctatetraene (or tridecacyclene; 1), originally reported by Scott et al. in 2000 as a byproduct for making a part of fullerene fragment,[7] has COT unit at the center of molecule (Scheme 2). Recently it was shown that two-electron reduction of compound 1 gave its aromatic dianion by Whalley et al.^[8] This is the analogous 10π Hückeloid.^[9] We have been interested in the aromaticity relocation in the polycyclic aromatic hydrocarbons (PAHs) upon the oxidation and demonstrated the sterically hindered pyrenes and perylenes could be oxidized with SbCl5 to give the persistent cations and dications.^[10] We have also succeeded in synthesis of the carbon-nanosheet, tetrabenzoperipentacene, which was obtained by the oxidative annulation reaction of the tetranaphthylpyrene derivative.[11] During our research to make a new COT containing carbon-nanosheet 2 from the naphthyl compound 1 upon oxidative conditions, we happened to discover the unique transformation of COT unit.



Scheme 2. Synthetic attempt to make nanographene 2 from compound 1.

Results and Discussion

We tried the annulation reaction of tridecacyclene **1** with iron chloride to synthesize compound **2** with planar COT structure. After several attempts, however, we failed to obtain the compound **2** and could isolate unexpected compound **3** in 69% (Scheme 2). High-resolution spiral-MALDI time-of-flight mass spectroscopy detected the parent ion peak at m/z = 633.1874, which was larger by 32 mass units than that of **1**. The ¹H NMR

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spectrum indicates lowering of symmetry of the product compared with **1**, featuring 10 doublet peaks and 5 triplet peaks that correspond to the 1,3- and 2-naphthyl protons, respectively, thus indicating the generation of the C_2 symmetric structure (Supporting Information, SI; Figure S1). The final structural determination of **3** was unambiguously obtained by X-ray analysis (Figure 1a).^[12] Surprisingly, the number of carbon atoms at the central ring reduced from 8-membered ring to 7-membered one, and the compound **3** has cycloheptatriene skeleton with spirolactone. To the best our knowledge, this is the first spiro[5.6]lactone cycloheptatriene compound.



Figure 1. a) Single crystal X-ray structure and chemical structure of **3.** b) Single crystal X-ray structure of **3H**·BF₄.Thermal ellipsoids are scaled at 50% probability. Solvent molecules are omitted for clarity.

Although the detailed reaction mechanism is uncertain at this moment, we believe that Scheme 3 can explain a plausible mechanism for the rearrangement of tridecacyclene **1** to compound **3**. First, the compound **1** was oxidized by FeCl₃ to form the cation radical, which reacts with molecular oxygen. The rearrangement occurs as illustrated, then, dioxirane formation-decomposition^[13] generates cycloheptatriene with spirolactone. Another possibility includes that the oxidation with molecular

oxygen induces the bond exchanges and the pinacol-type rearrangement generates cycloheptatriene (Scheme S1).^[14] We confirmed that this conversion was accelerated under the O_2 atmosphere and suppressed under an inert atmosphere or without FeCl₃.



Scheme 3. A plausible reaction mechanism of 1 to 3: Dioxirane formationdecomposition route.

The spirolactone structure is a bicyclic ester that is typically contained in fluoresceins.^[15] This can be performed as a reversibly switching unit with close/open ring, responding the ambient environment (ex. pH etc.). Thus, we expected that the addition of an acid to the compound **3** would open the spirolactone to form tropylium cation accompanying drastically change of its physical properties.

We measured UV-vis absorption and fluorescence spectra of the spirolactone **3** in THF (Figure 2). The compound **3** shows the featureless absorption at around 500 nm and the absorption peaks at 348 and 360 nm. Fluorescence of **3** exhibits at 603 nm and the fluorescence quantum yield (Φ_F) is 3%. Upon the addition of 30 eq. of trifluoromethanesulfonic acid (TfOH), the protonated compound **3** (**3H**·OTf) showed new absorption peaks at 466 and 532 nm. The fluorescence of **3H**·OTf exhibits intensive and slightly red shifted peak at 620 nm. The Φ_F of **3H**·OTf is 15%, becoming five times larger than that of the neutral compound **3**. The addition of HBF₄ into **3** also gave similar result (Figure S9). The spectral change was recovered by the addition of 30 eq. of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as a base.



Figure 2. UV-vis (solid line) and fluorescence (broken line) spectra of **3** (black) and **3H**-OTf (red) in THF. [**3**] = 1.6×10^{-5} M. For **3H**, 30 eq. of TfOH was added. Fluorescence spectra were taken for excitation (λ_{ex} = 500 nm) with the absorbance adjusted at 0.1.

To confirm the close/open ring structures, ¹H NMR spectrum of 3 with TfOH in THF-d₈ was measured at 183 K (Figure S3). The spectrum of 3H·OTf drastically changed especially for naphthalene ester moiety compared to that of the compound 3. The proton of the carboxylic acid was detected at 11.33 ppm, reflecting the hydrogen bonding. The diatropic ring current of the central tropylium was indicated by the down-field shift of H^a denoted in Figure 2 (7.78 ppm; $\Delta\delta$ from **3** = 0.4 ppm). These observations clearly prove the formation of the aromatic tropylium structure. The structure of the tropylium salt 3H·BF₄ was determined by single crystal X-ray diffraction analysis (Figure 1b).^[16] The crystal structure of 3H·BF₄ showed opened spirolactone. Also the compound 3H·BF4 in the crystal forms the dimer via hydrogen bonding between carboxylic acid. Based on the crystal structure of 3, we confirmed the C=C bonds of the 7membered ring are localized at three positions and two single bonds are connected to the spiro carbon (Figure 3). On the other hands, the C-C bond distances of the tropylium 3H·BF4 are delocalized at all the 7-membered ring. The mean-plane deviation of the tropylium part is 0.12 Å that is much smaller than that of 3 (0.26 Å). To evaluate the aromatic character of the 7-membered rings of 3 and $3H^+$, we calculated the nucleus independent chemical shift (NICS)^[17] based on the crystal structures at the HF/6-31G+(d,p) calculation level (Figure 3).[18] While the NICS values of the compound 3 are negligible, those of the tropylium 3H⁺ vary from -4.26 ppm (NICS(0)) to -7.15 ppm (NICS(+1)), clearly indicating the aromatic character. Another indicator of aromaticity, harmonic oscillator model of

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aromaticity (HOMA)^[19] also suggests its enough aromaticity (0.59).

To further understand the electronic features, the density functional theory (DFT) and the time-dependent (TD)-DFT calculations both at the B3LYP/6-31G(d) level using the Gaussian 09 software package were carried out (Figure 4).^[20] The HOMO and LUMO are non-degenerative and the coefficient distribution patterns in these frontier MOs appear delocalized over the entire molecule. The longest band of **3H**⁺ at 532 nm mainly comprises the transition from HOMO to LUMO (oscillator strength, *f* = 0.046), whereas the main absorption band at around 466 nm is composed of transitions from HOMO-1 to LUMO+1 (*f* = 0.12) and from HOMO-2 to LUMO+1 (*f* = 0.14). The transition energies and oscillator strengths simulated by TD-DFT calculations showed a good agreement with the observed absorption spectrum of **3H**·OTf (Figure S16).



Figure 3. a) Bond lengths and HOMA values of 3 (black) and $3H \cdot BF_4$ (red) based on the X-ray structures. b) NICS values of $3H^+$ calculated at the HF/6-31G+(d,p) level.



Figure 4. MO diagram of $\mathbf{3H}^*$ based on calculations at the B3LYP/6-31G(d) level.

Curiously precedents teach us that the oxidation of cycloheptatriene acids (thus tropylium cations) gives benzaldehyde or benzoic acid.^[1,21] According to these reports, we tried further oxidation of **3**. To a CH_2Cl_2 solution of the compound **3** at room temperature was added 5 equiv. of FeCl₃ at once. We monitored reaction profiles by an atmospheric pressure chemical ionization (APCI) mass spectroscopy, then detected $[M]^* = 451.22$ and 198.70, which correspond to decacyclene **4**⁷ and 1H,3H-benzo[*de*]isochromene-1,3-dione (**5**), respectively (Scheme 4, and Figure S10). These products **4** and **5** were confirmed by ¹H NMR spectrum (Figure S11) and we determined the conversion yield of **4** in 40%. A plausible reaction mechanism is shown in Scheme 4.



Scheme 4. Further oxidation of 3 with FeCl₃ along with a plausible reaction mechanism to 4 and 5.

In this reaction, the aromatic tropylium cation (7-membered ring) shrinks to 6-membered ring by division to release **5**. The driving force of this unique splitting could be the achievement of the stronger aromaticity.

Conclusions

In summary, we discovered the transformation of the nonaromatic COT into the cycloheptatriene spirolactone upon the oxidation, which could be reversibly interconverted to the aromatic tropylium cation by acid/base. This transformation of COT was operated not only by chemical reaction but also by electrochemical manipulation; a CH₂Cl₂ solution of the compound **1** was applied to voltage at 0.48 V vs Fc/Fc⁺ for 2 h and the absorption spectrum changed to that of **3H**⁺ (Figure S18). The original phenomenon of the ring-shrinking was observed by pristine COT, but we could characterize all the key molecular structures by X-ray analysis. In addition, the resultant cycloheptatriene could be converted to benzene upon further oxidation. Consequently, the π -conjugated ring size shrinks from 8 to 7 then 6 upon oxidation, directing to the stronger aromatization.

Experimental Section

1. Instrumentation and Materials

¹H NMR (400 MHz or 300 MHz) and ¹³C NMR (100 MHz) spectra were recorded with JEOL JNM-ECX 400 and 300 spectrometers at ambient temperature by using tetramethylsilane as an internal standard. The highresolution MS were measured by a JEOL JMS-700 MStation spectrometer and a BRUKER Autoflex II MALDI TOF MS. The highresolution APCI MS were performed on a BRUKER DALTONICS micrOTOF using positive and negative ion modes. UV/Vis absorption spectra were measured with a JASCO UV/Vis/NIR spectrophotometer V-570. X-ray crystallographic data for 3 were recorded at 100 K on a Rigaku R-AXIS RAPID/S using Mo-Kα radiation, and the data for 3H·BF₄ were recorded at 90 K with a BRUKER-APEXII X-Ray diffractometer equipped with a large area CCD detector. CV measurements were conducted in a solution of 0.1 M TBAPF₆ in dry dichloromethane with a scan rate of 100 mV/s at room temperature in an argon-filled cell. A glassy carbon electrode and a Pt wire were used as a working and a counter electrode, respectively. An Ag/Ag⁺ electrode was used as reference electrodes, which were normalized with the half-wave potential of ferrocene/ferrocenium⁺ (Fc/Fc⁺) redox couple. TLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. All other solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification. For spectral measurements, spectral-grade chloroform was purchased from Nacalai Tesque.

2. Experimental Section

3H-Spiro[benzo[de]isochromene-1,10'-cyclohepta[1,2-a:3,4-a':5,6-

a"]triacenaphthylen]-3-one (3): Compound 2 (10 mg, 0.016 mmol) was dissolved in CH₂Cl₂ (5 ml) under atmosphere. FeCl₃ (32 mg, 0.16 mmol) dissolved in CH_3NO_2 (0.5 ml) was added dropwise. After the reaction mixture was stirred at r.t. for 4 h, it was added to water and extracted with CH₂Cl₂. The organic phase was dried over Na₂SO₄ and concentrated. The crude product was separated by silica gel column chromatography (AcOEt/Hex=1:3) to give the compound 3 as red solid (7.0 mg, 0.011 mmol, 69%). The product was further purified by recrystallization (CH₂Cl₂/Hex). ¹H-NMR (600 MHz, CDCl₃): δ = 8.85 (d, J = 7.6 Hz, 2H), 8.46 (dd, J = 7.6, 1.4 Hz, 1H), 8.19 (d, J = 6.9 Hz, 4H), 8.02 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.2 Hz, 1H), 7.84 (t, J = 7.8 4H), 7.71 (q, J = 7.8 Hz, 4H), 7.61-7.49 (m, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 7.3 Hz, 1H) and 6.47 (t, J = 7.8 Hz, 1H) ppm; ¹³C-NMR (100 MHz, CDCl₃): $\delta = 166.06$, 138.07, 137.66, 137.48, 137.38, 136.50, 133.78, 132.31, 131.51, 129.49, 129.29, 129.13, 128.79, 128.77, 128.63, 128.23, 128.14, 128.02, 127.91, 127.87, 127.57, 127.03, 125.93, 125.58, 125.29, 124.99, 124.91, 120.91 and 89.39 ppm; HR-MS (Spiral MALDI): m/z: calcd for C48H25O2, 633.1849 $[M+H]^+$; found: 633.1874; UV-vis (THF): λ_{max} (ε $[M^{-1} \text{ cm}^{-1}]$) = 348 (31997), 360 (32000), and 491 (6637) nm; m.p. > 300°C.

3H: ¹H-NMR (400 MHz, THF- d_8 with 1 µl of TfOH): δ = 9.16 (d, J = 7.3 Hz, 2H), 9.09 (d, J = 7.3 Hz, 2H), 8.70 (d, J = 8.1 Hz, 2H), 8.65 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.1 Hz, 2H), 8.44 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 8.1 Hz, 2H), 8.20 (q, J = 7.4 Hz, 4H), 7.95 (d, J = 7.7 Hz, 1H), 7.80 (d, J = 7.0 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 7.0 Hz, 1H), 7.46 (t, J = 7.9 Hz, 2H) and 6.18 (d, J = 7.7 Hz, 2H) ppm; ¹³C-NMR (100 MHz, THF- d_8) δ = 169.32, 151.16, 150.69, 150.50, 147.69, 135.66, 135.36, 135.11, 134.83, 134.52, 133.73, 133.70, 133.36, 132.71, 132.12, 132.09, 131.91, 131.85, 131.77, 131.62, 131.30, 131.06, 130.88, 129.88, 129.28, 129.20, 128.99, 128.76, 128.38, 126.86, 126.14, 121.32 and 119.20 ppm; m.p. > 300°C.

Compound **3** (10 mg, 0.016 mmol) was dissolved in CH_2Cl_2 (4 ml) under atmosphere. FeCl₃ (18 mg, 0.080 mmol) dissolved in CH_3NO_2 (0.5 ml) was added dropwise. After the reaction mixture was stirred at r.t. for 4 h, it was added to water and extracted with CH_2Cl_2 . The organic phase was dried over Na_2SO_4 and concentrated. The crude product was separated by silica gel column chromatography (AcOEt/Hex=1:3) to give the unreacted **3** (5.4 mg), the compound **4** as yellow solid (2.9 mg, 0.006 mmol, 40% in conversion yield), and compound **5** as pale yellow solid (1.9 mg, 0.010mmol, 60% in conversion yield).

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Keywords: Cyclooctatetraene • Oxidation • π -Conjugation • Aromaticity • Rearrangement

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Entry for the Table of Contents

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We found that the modified cyclooctatetraene transforms into a cycloheptatriene spirolactone upon oxidation, which could be converted to benzene upon further oxidation. Consequently, the π -conjugated ring size shrinks from 8 to 7 then 6, directing to the stronger aromatization.



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Page No. – Page No.

Contraction of π -Conjugated Rings upon Oxidation from Cyclooctatetraene to Benzene via Tropylium Cation

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