

A Short-Step Synthesis of *syn*-1,6:8,13-Dimethano[14]annulene Dicarboximides

Mitsunori Oda^{1,*}, Miyako Neha¹, Yoshimitsu Kumai¹, Akira Ohta¹,
Ryuta Miyatake^{2,*}, Yanmei Zhang³, Shigeyasu Kuroda³

¹Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto, Nagano, Japan

²Centre for Environmental Conservation and Research Safety, University of Toyama, Toyama, Japan

³Department of Applied Chemistry, Graduate School of Science and Engineering, University of Toyama, Toyama, Japan

Abstract Double aldol condensation of cyclohepta-1,3,5-triene-1,6-dicarbaldehyde (**5**) with glutaraldehyde in the presence of piperidine in AcOH furnished bicyclo[5.4.1]dodeca-1(11),2,5,7,9-pentaene-3,5-dicarbaldehyde (**12**), presenting an alternative shortcut method for preparation of **12**. Reaction of dialdehyde **12** with phosphorane reagent **6a** in AcOH yielded mono- and double-Wittig adducts, **15** and **16**. The mono-adduct **15** undergoes intramolecular cyclization under basic conditions to give the title dicarboximide **10a**. Reactions of **12** with phosphorane reagents, **6a** and **6b**, under basic conditions resulted in direct formation of **10a** and **10b**, respectively. It is worthy to note that a dimethano[14]annulene derivative can be synthesized in two steps from **5**. Results of X-ray diffraction analysis and spectroscopic properties of **10a** are also described.

Keywords [14]Annulene, Bridged annulene, Aldol condensation, Wittig reaction, Dicarboximide

1. Introduction

We recently reported short-step syntheses of *N*-substituted 1,6-methano[10]annulene-3,4-dicarboximides (**1**) and their benzene-, thiophene- and naphthalene-annulated compounds, (**2–4**). [1] The annulenedicarboximides **1** were obtained in good yields from cyclohepta-1,3,5-triene-1,6-dicarbaldehyde (**5**) by its condensation with phosphorane reagents **6** in refluxing acetic acid (AcOH), providing an improved synthetic process from **5** to **1** compared with previously reported methods. [2–3] The annulene-dicarboximides annulated by an aromatic ring, **2–4**, were obtained from their corresponding annulated dicarbaldehydes **7–9** by their condensation with **6** under basic conditions (Scheme 1). In this paper, we describe an application of this efficient strategy with phosphorane reagents **6** to short-step synthesis of the title compounds **10**, novel dicarboximides with a π -extended [14]annulene skeleton bridged by two methylene groups. [4–5] Also, the solid-state structure and spectroscopic properties of **10a** are disclosed.

2. Results and Discussion

2.1. Synthesis of *syn*-1,6:8,13-dimethano[14]annulene Dicarboximides

We planned a synthetic route to the title compounds **10** from **5** via bicyclic dialdehyde **12**, as shown in Scheme 2. Vogel *et al.* reported synthesis of **12** in three steps from **5**, involving Horner-Wadsworth-Emmons (HWE) olefination [6] to yield diester **13**, subsequent DIBAL (diisobutylaluminium hydride) reduction and final oxidation with DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone), as shown in Scheme 3. [5] The structure of **12** was confirmed to have *syn*-stereochemistry between two methylene groups by X-ray crystallographic analysis. [7] In this study, we examined a modified method for preparation of **12**.

According to the method developed first by Lepage *et al.* [8] and later modified by us, [1] **5** was subjected to the direct double aldol condensation reaction with glutaraldehyde (**11**) in the presence of piperidine in AcOH (Scheme 4) to produce **12** in 34% yield, which is the same as the total yield of three steps reported by Vogel *et al.* The yield is greater than that (8%) of bicyclic benzene-annulated dialdehyde, reported by Lepage *et al.* [8] Our procedure for **12** is superior to the Vogel's method because of its one-pot procedure and that it can be carried out with commercially available glutaraldehyde instead of the HWE reagent which is required to prepare. With dialdehyde **12** in a hand, its reactions of **12** with phosphorane reagents **6** were examined next. Upon heating with **6a** in AcOH, **12** reacts to give mono- and double-Wittig adducts, **15** and **16**, in 60% and 9% yields, respectively (Scheme 4). [9] This

* Corresponding author:

mituoda@shinshu-u.ac.jp (Mitsunori Oda)

14sm302b@shinshu-u.ac.jp (Ryuta Miyatake)

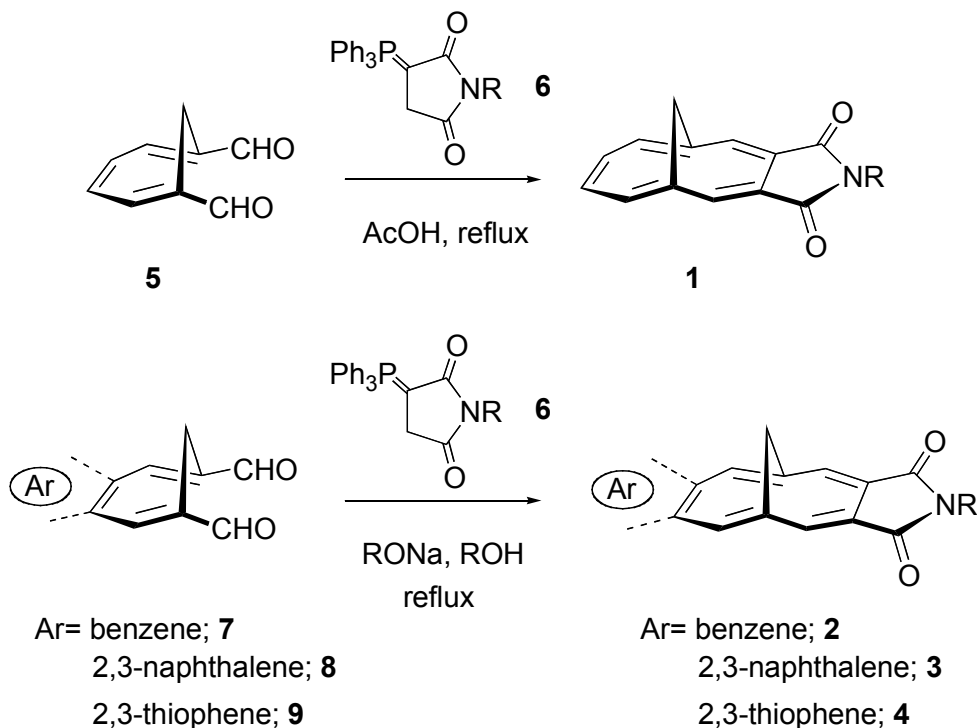
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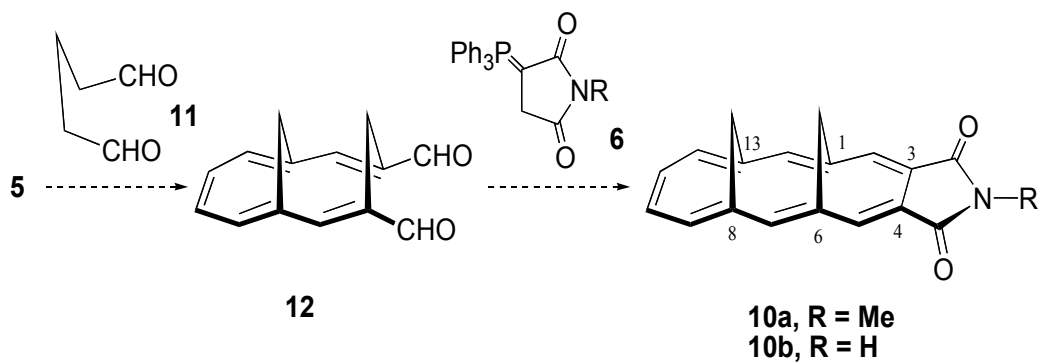
result is in contrast to that in the case of **5**, which reacts with **6** under the same acidic conditions to give the cyclized annulene product **1** (Scheme 1). Difficulty of cyclization of **15** under acidic conditions [1] may be ascribed to the relatively longer distance between two carbonyl carbon atoms in **12** than that in **5** (Fig. 1). [10]

Synthesis of **10a** from the adduct **15** was achieved by intramolecular aldol-type condensation under basic

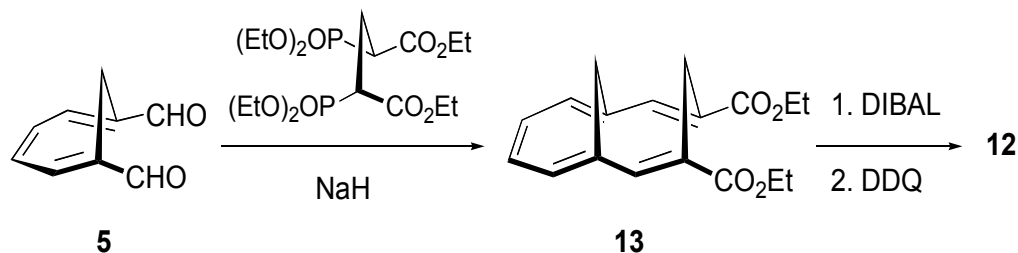
conditions. Treatment of **15** with sodium methoxide in methanol resulted in 86% yield of **10a**. Also, **10a** was obtained in 42% yield directly from **12** by reaction with **6a** under the basic conditions, and **10b** was synthesized in 52% yield similarly from **12** with **6b** (Scheme 5). Thus, it is demonstrated that **10a-b** can be obtained in two steps from **5**.



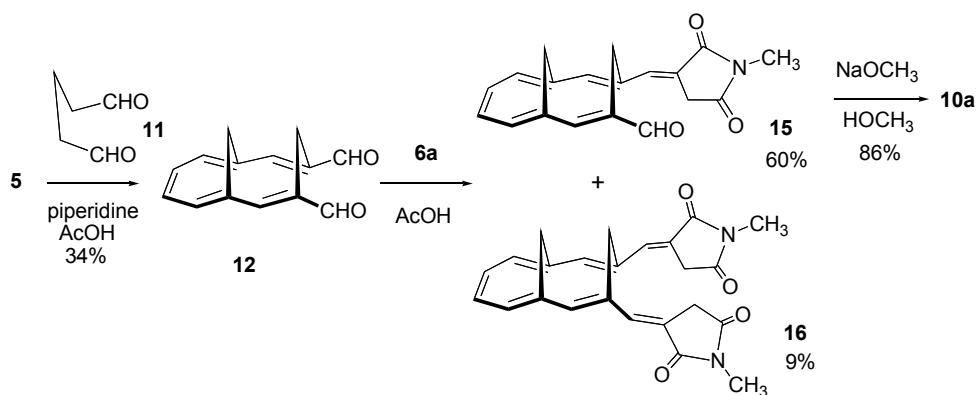
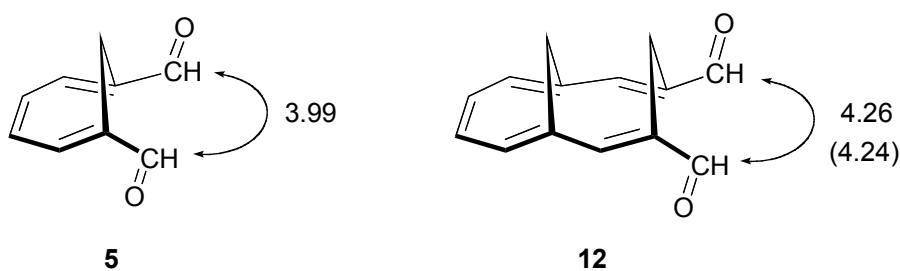
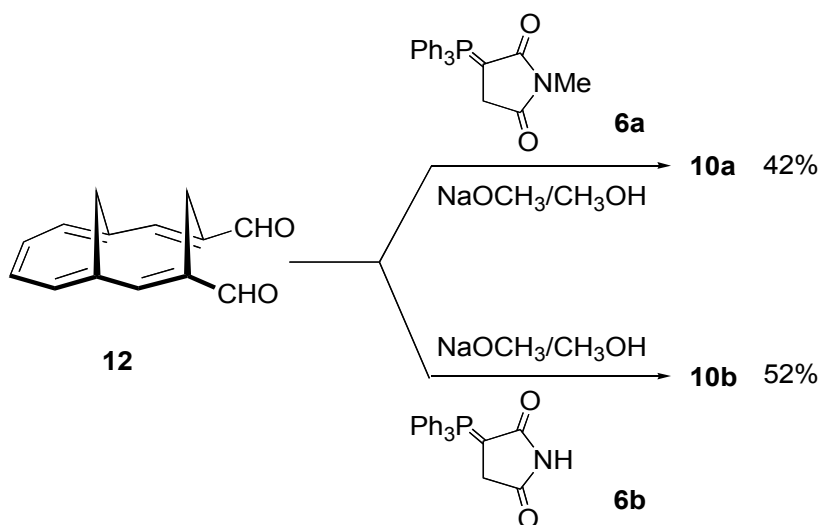
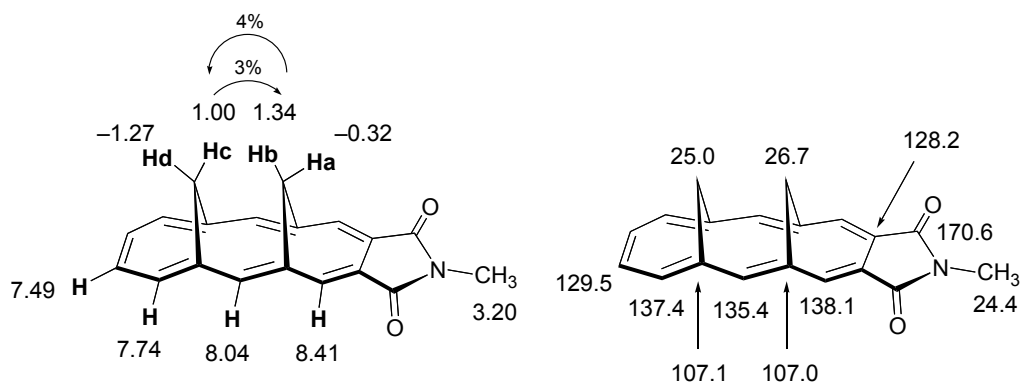
Scheme 1. Synthetic methods for various 1,6-methano[10]annulene-3,4-dicarboximides and their aromatic ring-fused compounds



Scheme 2. A short-step synthetic plan for *syn*-1,6:8,13-dimethano-[14]annulene-3,4-dicarboximides **10a-b**



Scheme 3. A reported synthetic way to **12** via **13** by Vogel *et al*

Scheme 4. Synthesis of **10a** via **12** and **15** from **5**Figure 1. Calculated distances (Å) between two carbonyl carbon atoms for **5** and **12**. A value in a parenthesis is taken from the X-ray structureScheme 5. One-pot synthesis of **10a-b** from **12**Figure 2. ¹H and ¹³C signal assignment (δ_{ppm}) for **10a** and results of NOE experiments indicated in %

2.2. Structure and Properties of *syn*-1,6:8,13-dimethano[14]annulene Dicarboximides

Compounds **10a–b** were obtained as orange crystals. Assignment of NMR signals and results of NOE experiments for **10a** are shown in Fig. 2. [11] The *syn*-stereochemistry of two methylene bridges in **10a**, expected by the stereochemistry of the starting dialdehyde **12**, was confirmed by NOE correlation between the inner hydrogen atoms, Hb and Hc, and also by X-ray diffraction analysis (*vide infra*). The hydrogen atoms at the methylene bridges were observed shielded by the aromatic [14]annulene ring, but resonate at slightly lower field ($\delta_{av.} = 0.75$ ppm) compared with those of the parent hydrocarbon, *syn*-1,6:8,13-dimethano[14]annulene (**17**) ($\delta_{av.} = -0.09$ ppm). Since the low field shift was observed only for Ha and Hb in **10a**, this shift is probably indebted to a deshielding effect of the carbonyl groups in the dicarboximide moiety. The structure of **10b** was similarly supported by spectroscopic analyses. The solid-state structure of **10a** was determined by X-ray diffraction analysis. ORTEP drawings are shown in Fig. 3. The *syn*-stereochemistry between two methylene bridges is seen clearly in the side view of ORTEP drawings. Average distance of two inner hydrogen atoms is estimated to be 1.638 Å, which is slightly shorter than that (1.78 Å) in **17**. [12] An average length of C–C bonds in the [14]annulene ring of **10a** (1.396 Å) and its deviation (± 0.028 Å) are very similar to those found in **17** (1.392 Å, ± 0.027 Å) [13], indicating that annulation of the imide ring on the [14]annulene ring does not affect the bond-convergency of the [14]annulene ring, as seen in **1**. [1]

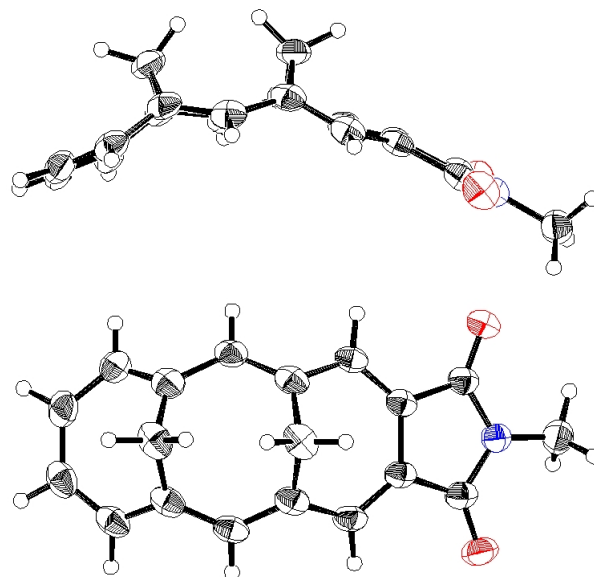


Figure 3. ORTEP drawings of one of two different molecules of **10a** in a cell. A side view (top) and top view (bottom). Oxygen atoms are shown in red and nitrogen atoms in blue

The UV-vis and emission spectra of **10a** in CH₃OH is shown in Fig. 4. The longest wavelength absorption of **10a** was found at λ_{max} of 530 nm, which shows a large red-shift compared with that (420 nm) of methano[10]annulene **1** (R = CH₃) and that (436 nm) of the isoelectronic methanobenzo[10]annulene **2** (R = CH₃). Upon photo-excitation **10a** emits light at 554 nm. However, its emission quantum yield ($\Phi = 1.7\%$) [14] is less than those of **1** (R = CH₃, $\Phi = 9.7\%$), **2** (R = CH₃, $\Phi = 10\%$) and *N*-butyl-2,3-anthracenimide ($\Phi = 46\%$). [15]

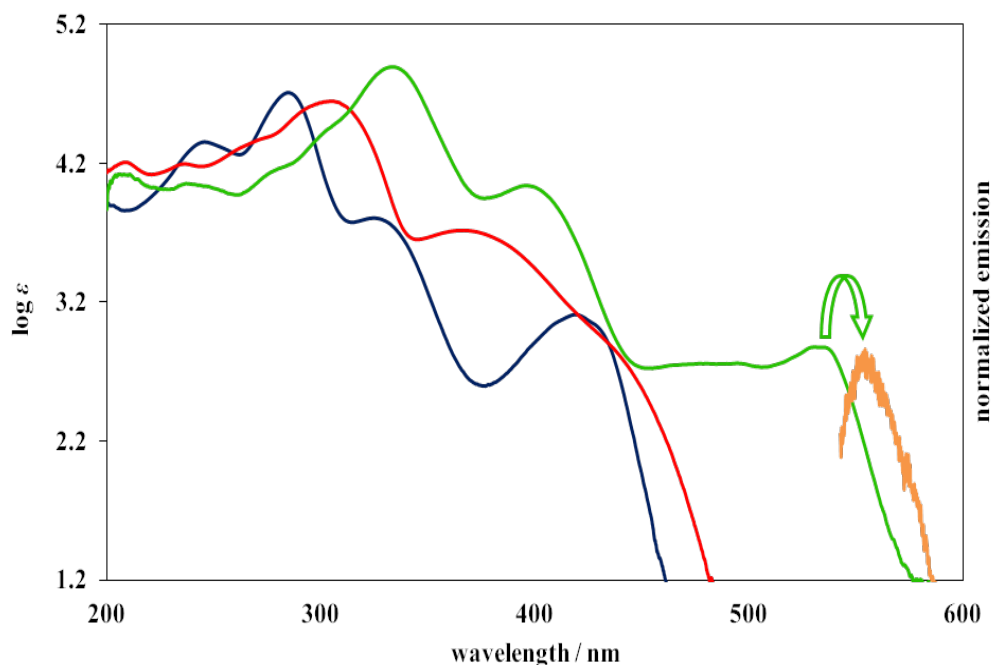


Figure 4. The UV-vis absorption spectra of **1** (R=Me, blue), **2** (R=Me, red), and **10a** (green) in MeOH and the normalized emission spectrum of **10a** (orange)

3. Experimental

3.1. General Remarks

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. ^1H - and ^{13}C -NMR spectra were recorded on JEOL λ 400 and ECA500 spectrometers. Chemical shift values of tetramethylsilane ($\delta = 0$ ppm) for ^1H -NMR spectra and CDCl_3 ($\delta = 77.0$ ppm) for ^{13}C -NMR spectra were used as internal standard. Mass spectra were measured on a JMS-700 mass spectrometer. Column chromatography was performed with Silica gel 60N from Kanto Chem. Glutaraldehyde (50% aqueous solution) and cyclohepta-1,3,5-triene were purchased from Sigma- Aldrich. Triphenylphosphine, maleimide, and *N*-methylmaleimide were purchased from Tokyo Chem. Ind. Cyclohepta-1,3,5-triene-1,6-dicarbaldehyde (**5**) was prepared from cyclohepta-1,3,5-triene in six steps according to the method of Vogel *et al.* [5, 16–17] Phosphorane reagents, *N*-methyl and unsubstituted triphenylphosphonylidenesuccimides, **6a** and **6b**, were prepared from triphenylphosphine and corresponding maleimides by our reported method. [1, 18]

3.2. Synthesis of bicyclo[5.4.1]dodeca-1(11),2,5,7,9-pentaene-3,5-dicarbaldehyde (**12**)

A 50% glutaraldehyde aqueous solution (2.00 g, 10.0 mmol) was added slowly to a refluxing solution of **5** (740 mg, 5.00 mmol) and piperidine (0.987 mL, 10.0 mmol) in 10 mL of AcOH under nitrogen atmosphere. After the addition, the resulted mixture was further refluxed for 4 h. The resulted dark brown reaction mixture was poured into cold water (200 mL) and was extracted with ether/hexane (30 mL x 4). The combined organic layer was washed with a saturated NaHCO_3 solution and brine, and was dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (ether/hexane = 15/85) to give 360 mg (34%) of **12** as yellow prisms. M.p. = 213–215 °C (lit. 215–216 °C). IR (KBr) ν_{max} = 1669 (s), 1655 (s), 1594 (s), 939 (s), 752 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 9.36 (s, 2H), 7.15 (m, 4H), 6.66 (s, 2H), 4.98 (d, J = 15.8 Hz, 1H), 4.13 (d, J = 12.2 Hz, 1H), 3.34 (d, J = 15.8 Hz, 1H), 0.66 (d, J = 12.2 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 193.0, 148.0, 132.0, 131.0, 123.0, 119.0, 28.5, 17.1 ppm.

3.3. Reaction of **12** with *N*-methyltriphenylphosphonylidenesuccimide (**6a**) in acetic acid

A mixture of dialdehyde **12** (212 mg, 1.00 mmol) and phosphorane reagent **6a** (373 mg, 1.00 mmol) in 5 mL of AcOH was refluxed on an oil bath for 19 h under nitrogen atmosphere. The resulted reaction mixture was poured into cold water (100 mL) and was extracted with chloroform (20 mL x 3). The combined organic layer was washed with a saturated NaHCO_3 solution and brine, and was dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography

(AcOEt/ CHCl_3 = 3/97) to give 179 mg (60%) of **15** and 36 mg (9%) of **16**.

15: Orange microcrystals, m.p. 210–212 °C. IR (ATR) ν_{max} = 1760 (m), 1691 (vs), 1658 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ = 9.32 (s, 1H), 7.15 (t, J = 2.0 Hz, 1H), 7.11 (dd, J = 10.3, 6.1 Hz, 1H), 7.10 (s, 1H), 7.06 (dd, J = 10.3, 6.1 Hz, 1H), 6.87 (d, J = 6.0 Hz, 1H), 6.83 (s, 1H), 6.71 (d, J = 6.1 Hz, 1H), 4.43 (dd, J = 21.8, 2.0 Hz, 1H), 4.41 (d, J = 15.8 Hz, 1H), 4.07 (d, J = 12.2 Hz, 1H), 3.80 (d, J = 15.8 Hz, 1H), 3.62 (dd, J = 21.8, 2.0 Hz, 1H), 3.09 (s, 3H), 0.49 (d, J = 12.2 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ = 194.2, 174.6, 171.7, 148.4, 139.5, 139.2, 131.9, 131.0, 130.0, 129.5, 123.5, 121.4, 120.9, 120.0, 117.6, 34.2, 28.2, 24.9, 22.1 ppm; UV-vis (CH_3OH) λ_{max} = 249 (log ϵ = 4.05), 312 (4.74), 397 (3.86) nm; MS (70 eV) m/z (rel int) 307 (M^+ , 100), 278 (29), 204 (15), 194 (20), 193 (68), 191 (23), 189 (15), 179 (36), 178 (57), 169 (32), 165 (37), 153 (18), 152 (24), 141 (20), 128 (15), 115 (16), 89 (15). HRMS Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_3$, 307.1208, found 307.1208.

16: Orange microcrystals, m.p. 298–300 °C. IR (ATR) ν_{max} = 1758 (s), 1689 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 7.12 (t, J = 2.0 Hz, 2H), 7.03 (m, 2H), 6.75 (s, 2H), 6.70 (m, 2H), 4.48 (d, J = 16.0 Hz, 1H), 3.91 (d, J = 12.5 Hz, 1H), 3.54 (dd, J = 21.5, 2.0 Hz, 2H), 3.45 (d, J = 16.0 Hz, 1H), 3.43 (dd, J = 21.5, 2.0 Hz, 1H), 3.09 (s, 6H), 0.36 (d, J = 12.5 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ = 173.8, 170.9, 138.8, 135.1, 130.2, 129.4, 123.1, 118.9, 116.5, 34.0, 33.5, 27.8, 24.9 ppm; UV-vis (CH_3OH) λ_{max} = 333 (log ϵ = 4.14), 407 (3.42) nm; MS (70 eV) m/z (rel int) 402 (M^+ , 20), 290 (14), 265 (20), 264 (100), 215 (22), 205 (20), 203 (16), 202 (20), 193 (15), 191 (18), 189 (18), 179 (23), 178 (23), 165 (31), 152 (17), 58 (15). HRMS Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4$, 402.1580, found 402.1580.

3.4. Synthesis of **10a** from **15**

To a solution of sodium methoxide (0.075 mmol) in 3 mL of methanol, prepared with 3.6 mg of 50% sodium hydride and methanol, was added 77.0 mg (0.25 mmol) of **15** in one portion. This mixture was refluxed on an oil bath for 5 h under nitrogen atmosphere. The resulted reaction mixture was poured into 0.1M HCl (40 mL) and was extracted with chloroform (15 mL x 3). The combined organic layer was washed with a saturated NaHCO_3 solution and brine, and was dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (AcOEt/ CHCl_3 = 1/99) to give 62 mg (86%) of **10a** as orange microcrystals.

M.p. 234–236 °C. IR (ATR) ν_{max} = 1752 (m), 1692 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ = 8.41 (s, 2H), 8.04 (s, 2H), 7.74 (m, 2H), 7.49 (m, 2H), 3.20 (s, 3H), 1.34 (d, J = 14.0 Hz, 1H), 1.00 (d, J = 13.5 Hz, 1H), –0.32 (d, J = 14.0 Hz, 1H), –1.27 (d, 13.5 Hz, 1H) ppm; UV-vis (CH_3OH) λ_{max} = 238 (log ϵ = 4.05), 278sh (4.15), 300sh (4.41), 334 (4.90), 396 (4.04), 465sh (2.72), 493 (2.77), 530 (2.89) nm; MS (70 eV) m/z (rel int) 289 (M^+ , 100), 274 (18), 204 (39), 203 (36), 202 (32), 189 (17). HRMS Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_2$, 289.1103, found 289.1099.

3.5. One-pot synthesis of **10a** from **12**

A mixture of **12** (21 mg, 0.10 mmol), **6a** (56 mg, 0.15 mmol) and sodium methoxide (8 mg, 0.15 mmol) in methanol (3 mL) was refluxed on an oil bath for 8 h under nitrogen atmosphere. The resulted reaction mixture was poured into 0.1M HCl (20 mL) and was extracted with chloroform (10 mL x 3). The combined organic layer was washed with a saturated NaHCO₃ solution and brine, and was dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (AcOEt/CHCl₃ =1/99) to give 12 mg (42%) of **10a** as orange microcrystals.

3.6. One-pot Synthesis of **10b** from **12**

A mixture of **12** (21 mg, 0.10 mmol), **6b** (54 mg, 0.15 mmol) and sodium methoxide (11 mg, 0.20 mmol) in methanol (3 mL) was refluxed on an oil bath for 8 h under nitrogen atmosphere. The resulted reaction mixture was poured into 0.1M HCl (30 mL) and was extracted with chloroform (10 mL x 3). The combined organic layer was washed with a saturated NaHCO₃ solution and brine, and was dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (AcOEt/CHCl₃ =1/9) to give 14 mg (52%) of **10b** as orange solids.

M.p. 186–188°C. IR (ATR) ν_{\max} = 1764 (s), 1752 (s), 1692 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 8.44 (s, 2H), 8.09 (s, 2H), 7.90 (br, 1H), 7.77 (m, 2H), 7.50 (m, 2H), 1.95 (d, *J* = 14.1 Hz, 1H), 0.97 (d, *J* = 13.2 Hz, 1H), -0.44 (d, *J* = 14.1 Hz, 1H), -1.22 (d, *J* = 13.2 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ = 170.1, 138.6, 137.7, 135.6, 129.6, 128.6, 107.1, 107.0, 26.3, 25.0 ppm; UV-vis (CH₃CN) λ_{\max} = 272 (log ϵ = 3.88), 300sh (4.31), 328 (4.85), 330 (4.86), 393 (3.94), 495 (2.67), 527 (2.80), 533 (2.79) nm; MS (70 eV) *m/z* (rel int) 275 (M⁺, 100), 260 (17), 204 (25), 203 (28), 202 (26), 189 (14), 101 (17). HRMS Calcd for C₁₈H₁₃NO₂, 275.0946, found 275.0947.

3.7. X-ray Diffraction Analysis of **10a**

Diffraction measurements were conducted using a Rigaku R-AXIS RAPID diffractometer at -100°C. Crystal data for **10a** are as follows; monoclinic, space group; *P*2₁/*n* (# 14), *a*; 9.32224(17) Å, *b*; 12.2859(3) Å, *c*; 24.6428(5) Å, β ; 90.3387(7)°, *V*; 2822.35(9) Å³, *Z*; 8, *R*; 0.0488, *wR*₂; 0.1225, *R*₁; 0.0448 (*I* > 2.00σ(*I*)), and *S*; 1.038. Tables of fractional atomic coordinates, thermal parameters, bond lengths, and angles have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom (CCDC 1048825) [Direct line: +44 1223 762910, Fax: +44 (0) 1233 336033, e-mail: deposit@ccdc.cam.ac.uk].

4. Conclusions

We have demonstrated an alternative shortcut synthesis

of dialdehyde **12** from **5** by double aldol condensation with glutaraldehyde and also accomplished synthesis of the title compounds **10a-b** from **12**. It should be stressed that a dimethano[14]annulene derivative can be synthesized in two steps from **5**. The solid-state structure of **10a** was determined by X-ray diffraction analysis, revealing that annulation of the dicarboximide moiety on a dimethano[14]annulene core does not affect bond-convergence of the annulene ring. Upon photoexcitation **10a-b** show emission but their quantum yields are less than those of **1** and **2**.

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was confirmed to be *E*-geometry in both **15** and **16** based on chemical shifts of their vinyl hydrogen atoms. For details of chemical shifts in related compounds, see in [1].

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