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Synthesis and Structure of Systems Containing Pyramidalized and Strained Double Bond: An Investigation on the Cycloaddition Reactions of *cis*- and *trans*-3,8-dicarbomethoxy-3,8-dihydroheptalene

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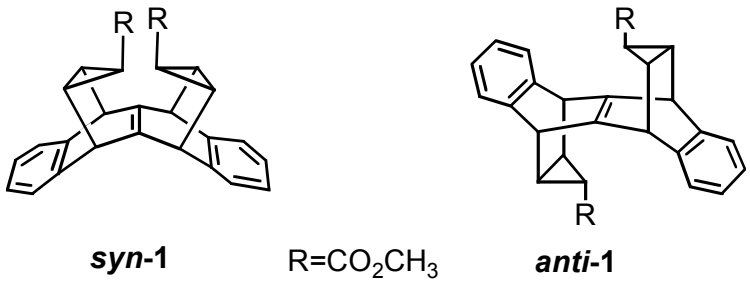
The cycloaddition reactions of *cis*-3,8-dicarbomethoxy-3,8-dihydroheptalene ***cis*-2** and *trans*-3,8-dicarbomethoxy-3,8-dihydroheptalene ***trans*-2** with various dienophiles such as dimethyl acetylenedicarboxylate (DMAD), p-benzoquinone, maleic anhydride, tetracyanoethylene, naphtoquinone gave monoaddition products **15-23**. Further addition of benzyne and dimethyl acetylenedicarboxylate to **18** resulted in the formation of the compounds ***syn*-25** and ***syn*-26** having pyramidalized double bonds. The addition of benzyne to 21 and the addition of dimethyl acetylenedicarboxylate to **21, 22** and **23** gave the anti configuration products ***anti*-26**, **27** and **28**, respectively. X-ray structures of ***syn*-25**, ***syn*-26** and ***anti*-26** show the pyramidalized angles to be 16.5°, 19.9° and 8.0°, respectively.

Introduction

Strain can be introduced in a molecule by distorting one or more chemical bonds from their "normal" bond lengths or bond angles[1]. Alkenes in which the double bonds are distorted or pyramidalized are of theoretical interest and usually present a considerable challenge with regard to synthesis[2]. Pyramidalized alkenes are molecules containing carbon-carbon bonds in which one or both of the sp^2 carbon atoms do not lie in the plane of the attached atoms[3]. Theoretical work has shown that a trigonal center of a double bond pyramidalizes when located in an asymmetrical environment[4]. Evidence for pyramidalization was first obtained in NMR studies on norbornadiene and has been substantiated by X-ray studies of crystalline norbornenes and sesquinorbornenes[5].



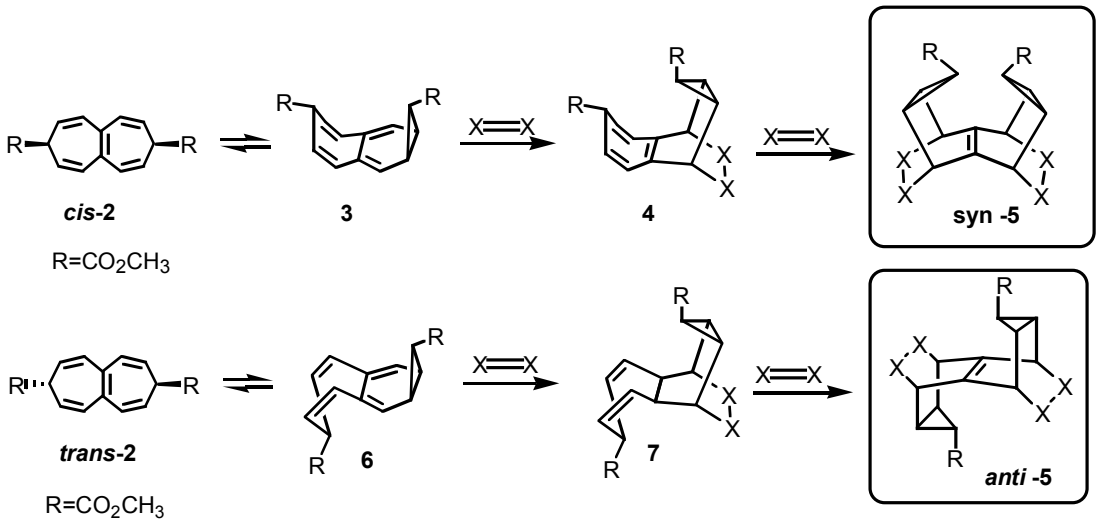
Scheme 1

Recently, we reported the synthesis of ***syn*-1**[6] and ***anti*-1**[7] (Scheme 1). Because the two faces of the double bond are equivalent in ***anti*-1** and the NMR is consistent with the C_2 axis of symmetry that lies along the C-C double bond, a planar equilibrium geometry at the double bonded carbon atoms is expected. X-ray diffraction analysis confirmed the planarity of the central double bond in ***anti*-1**. However, the crystal structure of ***syn*-1** showed the carbon atoms to be pyramidalized with a bend of 16.8° away from planarity.

We now report the synthesis of bisadducts similar to ***syn*-1** and ***anti*-1** from the reaction of ***cis*-2** and ***trans*-2** with various dienophiles. The pyramidalization of the central sp^2 carbon atoms and the reactivity of the formed adducts was investigated. Detailed synthesis of *cis*- and *trans*-dihydroheptalenes **2** is also described.

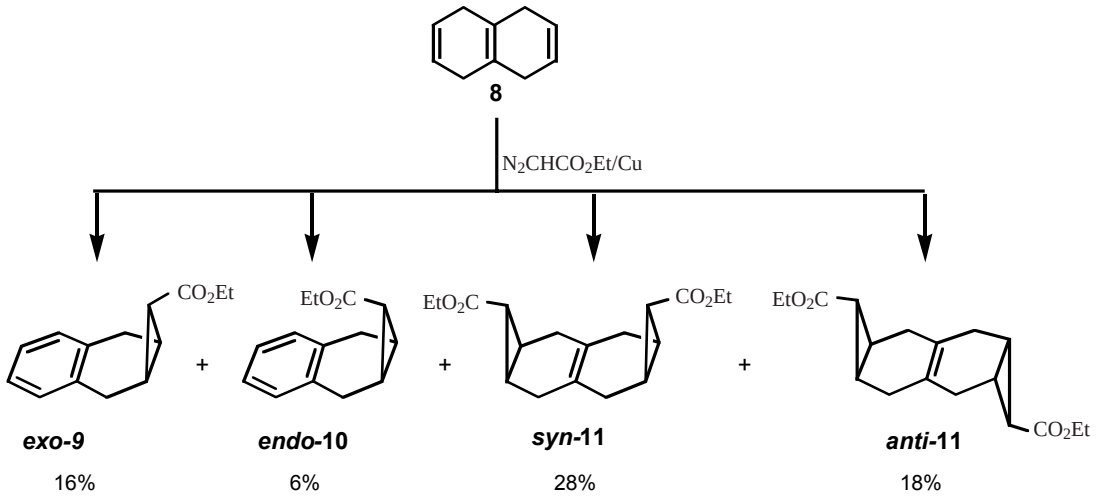
Results and Discussion

Construction of the *syn* and *anti* frameworks was achieved by the reaction of dienophile with *cis*- and *trans*-dihydroheptalene **2** as depicted in Scheme 1. For the synthesis of ***syn*-1** and ***anti*-1**, 2 moles benzyne were added to ***cis*-2** and ***trans*-2**, where advantage was taken of the cycloheptatriene-norcaradiene equilibrium (Scheme 2). It is well known that cycloheptatriene (CHT) is in equilibrium with its valence isomer, norcaradiene (NOR), and π-electron-withdrawing substituents at C-7 shift the CHT-NOR equilibrium in favor of NOR[8].



Scheme 2

Vogel and Hogrefe[9] reported that isotetralin reacts with excess ethyl diazoacetate to give the bis-adduct ***anti*-11** in a yield of 18%. ^{1}H-NMR studies have revealed that the reaction mixture is very complex. This mixture was subjected to silica gel column chromatography. We found that syn-isomer **11** was also present, in a total yield of 28%. Oxidation products **9** and **10** were also isolated and characterized (Scheme 3).



Scheme 3

The ^{1}H- and ^{13}C-NMR spectra of **9** and **10** were completely in agreement with the proposed structures. The exo and endo isomers **9** and **10** were distinguished on the basis of the coupling constant (J = 4.2 Hz) observed for the trans cyclopropane ring protons[10].

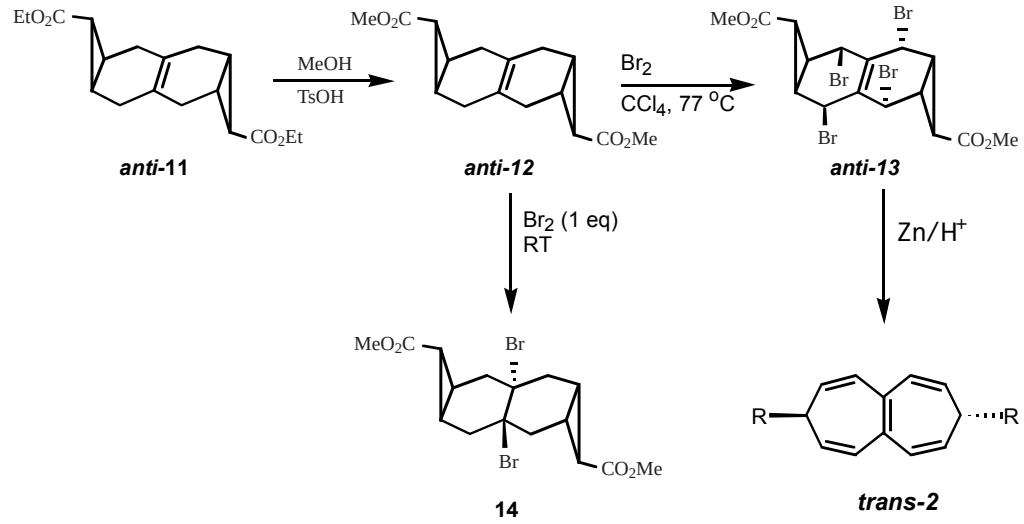
Products **9** and **10** are known and their synthesis was reported by Neidlein[11] and Kharicheva et al.[12] from the Cu catalyzed ethyl diazoacetate addition to dihydronaphthalene. The formation of these products can be explained by the aromatization of the initially formed mono-carbene addition products under the given reaction conditions. ***syn*-11** and ***anti*-11** were refluxed in methanol for three days in the presence of *p*-toluenesulfonic acid to give ***syn*-12** and ***anti*-12** methyl esters in high yields[6,7].

The high-temperature bromination technique of hydrocarbons developed by Balcı et al.[13] has proven to be a suitable way of synthesizing polyhalogenated hydrocarbons. Bromination of ***anti*-12** in CCl_4 at 77°C gave tetrabromo compound ***anti*-13**, while bromination in darkness and at room temperature resulted in the formation of **14** exclusively (Scheme 4). The isomer ***cis*-2** was synthesized as described before[7].

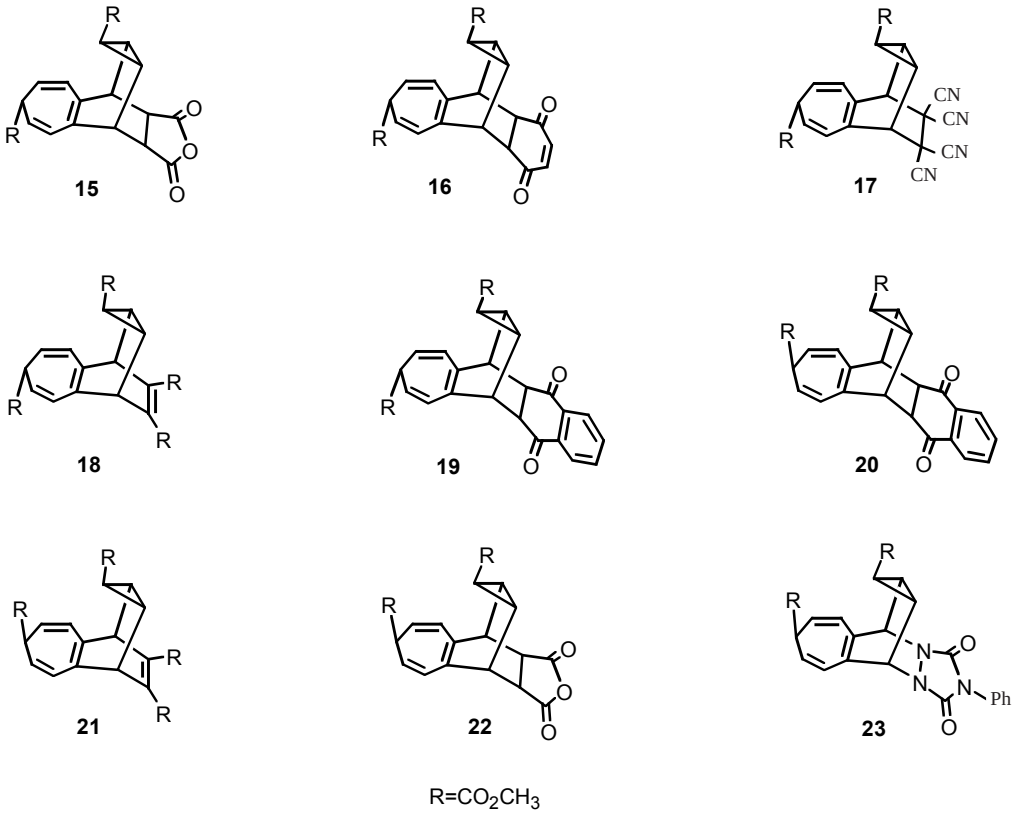
The *cis*-3,8-dicarbomethoxy-3,8-dihydroheptalene (***cis*-2**) was subjected to Diels-Alder cycloaddition with various dienophiles, such as maleic anhydride, *p*-benzoquinone, tetracyanoethylene, dimethyl acetylenedicarboxylate (DMAD) and naphthoquinone to form the corresponding Diels-Alder mono addition products **15, 16, 17, 18,** and **19**, whereas ***trans*-2** was reacted with naphthoquinone, dimethyl acetylenedicarboxylate, maleic anhydride and N-phenyltriazolinedion (PTAD) to give **20, 21, 22,** and **23** (Scheme 5).

Carefull examination of the ^{1}H- and ^{13}C-NMR spectra of the products showed exclusive formation of the norcaradien-type adducts (**15-23**), since bis-cycloheptatriene ***cis*-2** and ***trans*-2** are in equilibrium (Scheme 1) with their valence isomers **3** and **6**. We determined the presence of only the *exo* isomer (based

on the cyclopropane ring) on the basis of the measured coupling constants at the cyclopropane ring (J = 3-4 Hz). All dienophiles added to the valence isomer norcaradiene. The exclusive formation of the *endo* addition products is controlled by secondary orbital interaction. In all these reactions we observed a strong regio- and stereo-selectivity.

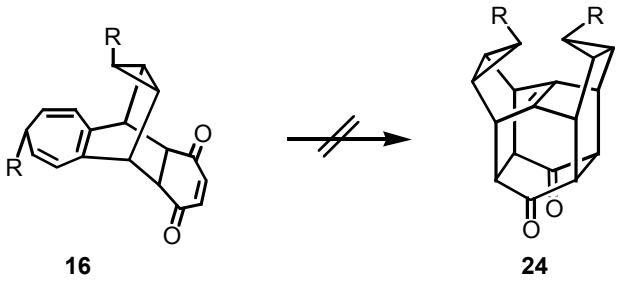


Scheme 4



Scheme 5

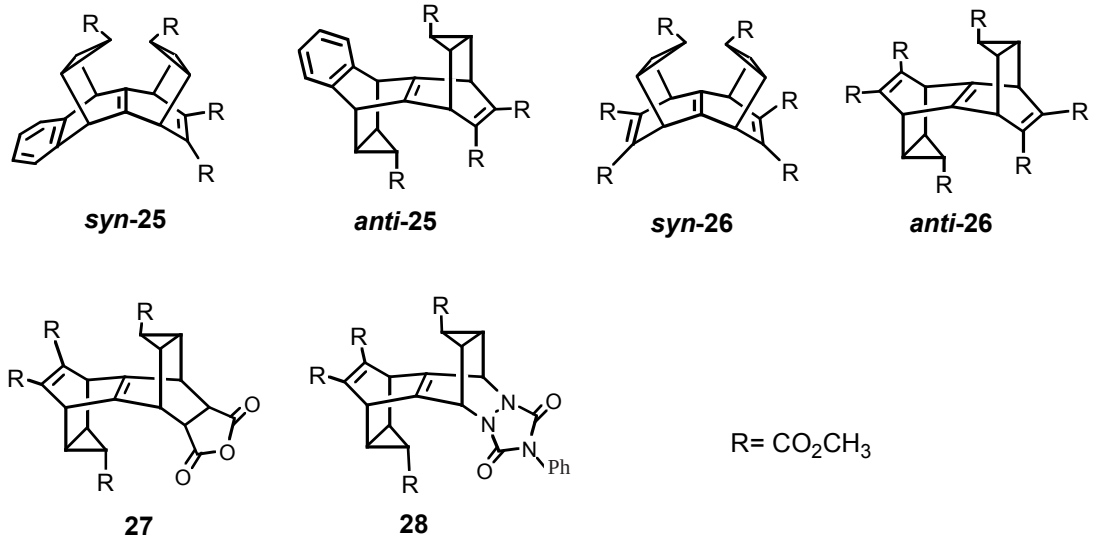
To examine the behavior of the second cycloheptatriene ring in **15-23**, in view of involvement in cycloaddition reactions, we tried to achieve an intramolecular cycloaddition reaction with compound **16** to entry to the corresponding cage molecule **24** (Scheme 6). All attempts failed. Inspection of the *Dreiding* models indicated that the quinone system is too far from the cycloheptatriene unit for any intramolecular cyclization reactions.



Scheme 6

The construction of ***syn*-25** and ***anti*-25** were carried out by the reaction of benzyne (generated from benzene diazonium-2-carboxylate hydrochloride[14]) as dienophile with mono-addition products **18** and **21**[7]. The structural assignment was made from the NMR data.

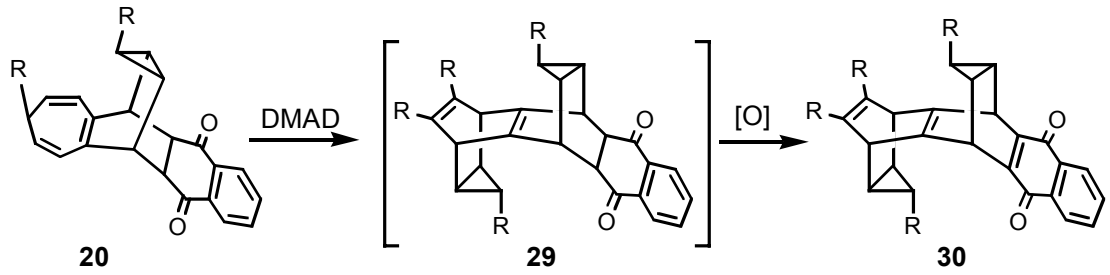
The symmetrical compounds ***syn*-26** and ***anti*-26** were prepared by the addition of two equivalents of dimethyl acetylenedicarboxylate to ***cis*-2** and ***trans*-2** without using solvent (Scheme 7). The ^{1}H-NMR spectrum of ***syn*-26** was very similar to that of ***anti*-26**, except that the resonance two cyclopropane protons (adjacent to ester group) in ***syn*-26** is shifted to a lower field (δ2.53 ppm) than the resonance in ***anti*-26** (δ = 0.94 ppm). We attributed this extraordinary shift to the steric compression between these two protons in ***syn*-26**.



Scheme 7

Dimethyl acetylenedicarboxylate was added to the systems **22**[7] and **23**[15], and the corresponding compounds **27** and **28** were obtained. Monocycloaddition product **20** was reacted with DMAD without

solvent, and compound **30** was obtained as the sole product (Scheme 8). The formation of **30** can be explained by the formation of the *anti*-bis adduct **29** followed by oxidation. The ^{13}C-NMR spectrum of **30** sets, especially the **10** carbon resonances in the olefinic region, conform to the proposed structure.



Scheme 8

The X-ray crystal structures of compounds ***syn*-25, *syn*-25** and ***syn*-26** were determined[16]. The pyramidalization angle can be obtained from the formula

$$\cos\phi = -\cos(R-C-C)/\cos 0.5(R-C-R)$$

The experimental ϕ values for ***syn*-25** and ***syn*-26** average 16.5° and 19.9° while the values for ***syn*-25** average 8°. Replacement of the benzene ring in ***syn*-1** with dimethyl acetylenedicarboxylate gave rise to a bending of 19.9° in the central double bond. This observation can be explained in terms of the aromatic carbon-carbon bonds being longer than those of the olefinic carbon-carbon double bonds. These data imply significant pyramidalization of the central sp^2 carbon atoms in ***syn*-25** and **26** and approximate planarity in ***syn*-25**. The pyramidalization arises from the steric interaction between the two hydrogen atoms.

Experimental Section

General. All solvents were dried and distilled by standard procedures. Melting points were determined with a capillary melting point apparatus (Thomas-Hoover). Infrared spectra were obtained from KBr pellets or solution in 0.1 mm cells on an infrared recording spectrophotometer. ^{1}H-NMR spectra were recorded on a 200 MHz spectrometer and are reported in δ units with TMS as the internal standard. All column chromatography was performed on silica gel (60-mesh, Merck) and Florisil 0.150-0.250 mm (60-100 mesh, ASTM).

Reaction of Isotetralin with Ethyl Diazoacetate: To a magnetically stirred suspension of isotetralin (44.4 g, 0.34 mol) and Cu powder (2.8 g) at 100°C, ethyl diazoacetate (112 g, 0.98 mol) was added dropwise within 48 h. After completion of the addition, the brown reaction mixture was cooled to room temperature and then 280 mL of ether was added. The etheral solution was allowed to stand for 12 h at -20°C. The formed precipitate, anti-bis-adduct **11** (13.4 g, 13%) and Cu powder, was removed by filtration and the solvent was evaporated. A part (4.0 g) of the residue (115.5 g) was subjected to silica gel (100 g) column chromatography, eluting with benzene/hexane (5:95). Elution gave compound **9** as the first fraction: **exo-Ethyl-3,4-benzobicyclo[4.1.0]hept-3-ene-7-carboxylate (9):** (376 mg, 16%): white needles, mp 44-45°C (Lit. mp[12]: 42-43°C), from hexane. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.15-6.99 (AA'BB' system, 4H), 4.09 (q, J=7.15 Hz, OCH_2, 2H), 3.11 (bd, A part of AB system, J=16.2 Hz, 2H), 3.10 (bd, b

part of AB system, J=16.2 Hz, 2H), 1.97 (m, 2H), 1.47 (t, J=3.9 Hz, 1H), 1.22 (t, J=7.1 Hz, $OCH_2\mathbf{CH}_3$, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 174.82, 134.10, 129.41, 126.94, 60.79, 28.70, 22.62, 19.26, 14.72; IR (KBr, cm^{-1}) 2960, 2900, 2820, 1715, 1450, 1370, 1340, 1300, 1270, 1160, 995, 750.

The second fraction: **endo-Ethyl-3,4-benzobicyclo[4.1.0]hept-3-ene-7-carboxylate (10):** (141 mg, 6%): mp 45-46°C, white needles from hexane. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.07 (bs, 4H), 3.76 (q, J=7.2 Hz, OCH_2, 2H), 3.19-2.99 (m, 4H), 1.72 (m, 3H), 1.08 (t, J=7.2 Hz, $OCH_2\mathbf{CH}_3$, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 171.40, 136.13, 128.96, 126.20, 60.41, 25.48, 21.47, 17.32, 14.50; IR (KBr, cm^{-1}) 2950, 2900, 1715, 1500, 1420, 1370, 1350, 1150, 940. The third fraction:***syn*-Diethyl tetracyclo[5.5.0.0^{3,5}.0^{9,11}]dodec-1(7)-ene-4,10-dicarboxylate (*syn*-11):** (894 mg, 28%): mp 79-80°C, white needles from hexane. The NMR spectrum was identical to that reported[6].

As the fourth fraction we isolated anti-bis adduct ***anti*-11** (192 mg, 5.2%)[9]. The isolated bis-carbene addition products ***syn*-11** and ***anti*-11** were converted to the corresponding methylesters ***syn*-12** and ***anti*-12** as described earlier[6,7].

Bromination of *anti*-12 at 77°C: Compound ***anti*-12** (5 g, 18.11 mmol) was dissolved in 250 mL of CCl_4 in a 500 mL two necked flask equipped with reflux condenser and inlet glass tube touching the bottom of the reaction flask. The inlet glass tube was connected to a 25 mL of round-bottom flask containing 13 g (81.25 mmol) of bromine. Bromine vapors were obtained by heating the flask to 100°C, and it was transferred directly to CCl_4 solution having a temperature of 77°C, for 10 min with magnetic stirring. The reaction mixture was refluxed for 1 h and the solvent evaporated, and then 50 mL of CH_2Cl_2 and 75 ml of hexane were added. The CH_2Cl_2/hexane solution was allowed to stand for 15 h at 20°C. Tetrabromide **13**[9] (8 g, 74.6%) was removed by filtration, dec. over 190°C.

Bromination of *anti*-12 at RT: To a magnetically stirred solution of compound ***anti*-12** (308 mg, 1.1 mmol) in 15 mL of dry CH_2Cl_2, a solution of bromine (175 mg, 1.1 mmol) in 5 mL CH_2Cl_2 was added dropwise for 5 min in darkness and at room temperature. The formed solution was stirred at RT for 30 min. The solvent was removed under reduced pressure. The residue crystallized from CH_2Cl_2/methanol to give the dibromide **14** (288 mg, 60%): colorless crystals, mp 144.5-145°C from CH_2Cl_2/methanol; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.67 (s, OCH_3, 6H), 2.69-2.13 (m, 12H), 1.86-1.26 (m, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 174.99, 69.55, 52.28, 39.94, 36.43, 25.02, 20.28, 19.93; IR (KBr, cm^{-1}) 2995, 2940, 2890, 2800, 1715, 1440, 1340, 1170, 990, 910.

Endo-5-*exo*-16-Dicarbomethoxy-12-oxopentacyclo[7.5.3.0^{2,8}.0^{10,14}.0^{15,17}]heptade- ca-2(8), 3,6-triene-11,13-dione (15). To a solution of ***cis*-2** (103 mg, 0.37 mmol) in 15 mL of $CHCl_3$, maleic anhydride was added (55 mg 0.56 mmol) at r.t. The solution was stirred at r.t. for 312 h. The solvent was evaporated and the residue crystallized from $CHCl_3$/ether to afford the endo adduct **15** as colorless crystals (125 mg, 89%), mp 205-207°C: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.04 (d, A part of AX system, J=8.6 Hz, 2H), 5.21 (dd, X part of AX system, J=8.6 Hz, J=5.7 Hz, 2H), 3.81 (s, OCH_3, 3H), 3.70 (m, 2H), 3.63 (s, OCH_3, 3H), 3.47 (bs, 2H), 2.35 (t, J=5.7 Hz, 1H), 1.86 (m, 2H), 1.15 (t, J=2.6 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 172.99, 172.38, 171.49, 135.64, 126.06, 112.76, 53.00, 52.53, 46.28, 43.40, 38.65, 21.24, 21.13; IR (KBr, cm^{-1}) 2960, 1775, 1740, 1720, 1440, 1300, 1255, 1220, 1160, 1060, 920, 910.

Endo-5-*exo*-17-Dicarbomethoxy-pentacyclo[7.4.3.0^{2,8}.0^{10,15}.0^{16,18}]octadeca-2(8), 3,6,12-tetraene-11,14-dione (16): *p*-Benzoquinone (500 mg, 1.83 mmol) and ***cis*-2** (310 mg, 2.87 mmol) were

dissolved in 15 mL $CHCl_3$. The solution was stirred at r.t. for 3 days, and the color of the reaction mixture turned from green to red. The solvent was evaporated and the residue purified by crystallization from $CHCl_3$/ether, giving the monoaddition product **16** (316 mg, 73%): yellow crystals, mp 195-197°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.51 (s, 2H), 5.85 (d, A part of AX system, J=8.4 Hz, 2H), 5.1 (dd, X part of AX system, J=8.4 Hz, J=5.1 Hz, 2H), 3.77 (s, OCH_3, 3H), 3.73 (m, 2H), 3.60 (s, OCH_3, 3H), 3.21 (bs, 2H), 2.23 (t, J=5.1 Hz, 1H), 1.87 (m, 2H), 0.99 (t, J=2.7 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 198.30, 173.38, 173.22, 141.77, 137.09, 126.20, 111.59, 52.80, 52.35, 49.35, 43.38, 41.99, 21.79, 18.73; IR (KBr, cm^{-1}) 3030, 2950, 1740, 1720, 1670, 1440, 1410, 1350, 1320, 1280, 1170, 1090, 870.

Endo-5-*exo*-11-Dicarbomethoxy-13,13,14,14-tetracyanotetra-cyclo[7.3.2.0^{2,8}.0^{10,12}] tetradeca-2(8),3,6-triene (17): Compound ***cis*-2** (317.5 mg, 1.16 mmol) and tetracyanoethylene (170 mg, 1.32 mmol) were dissolved in 15 ml of $CHCl_3$. The solution was stirred at room temperature for 1 day. The solvent was evaporated, and residue purified by crystallization from acetone/ether giving the monoaddition product **17** as colorless crystals (368 mg, 79%), dec. 215°C: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.32 (d, A part of AX system, J=8.9 Hz, 2H), 5.47 (dd, X part of AX system, J=8.9 Hz, J=5.6 Hz, 2H), 4.04 (m, 2H), 3.86 (s, OCH_3, 3H), 3.69 (s, OCH_3, 3H), 2.36-2.32 (m, 3H), 1.20 (t, J=2.9 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 172.09, 169.96, 133.73, 125.88, 115.89, 111.31, 111.06, 53.41, 53.22, 46.30, 43.73 (2C), 21.15, 15.92; IR (KBr, cm^{-1}) 3005, 2950, 1730, 1440, 1410, 1325, 1305, 1275, 1250, 1165, 1035, 945.

Endo-5-*exo*-11,13,14-Tetracarbomethoxy-tetracyclo[7.3.2.0^{2,8}.0^{10,11}]tetradeca-2(8),3,6,13-tetraene (18): A solution of ***cis*-2** (300 mg, 1.10 mmol) and dimethyl acetylenedicarboxylate (186 mg, 1.31 mmol) in 20 ml of $CHCl_3$ was stirred at 65°C for 16 days. The solvent was removed under reduced pressure. Chromatography on Florisil (25 g) eluting with ethyl acetate/hexane (250 mL, 6:94) gave the starting materials (120 mg, DMAD and ***cis*-2**). The second fraction (200 mL, EtOAc as eluent) afforded the monoadduct **18** (400 mg, 87.6%) as colorless liquid: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.13 (bd, A part of AX system, J=7.1 Hz, 2H), 4.09 (m, 2H), 3.87 (dd, X part of AX system, J=7.1 Hz, J=5.0 Hz, 2H), 3.77 (s, OCH_3, 6H), 3.71 (s, OCH_3, 3H), 3.56 (s, OCH_3, 3H), 3.21 (bs, 2H), 2.07 (m, 2H), 1.64 (t, J=5.0 Hz, 1H), 1.52 (t, J=2.8 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 174.82, 171.64, 166.41, 145.68, 135.96, 123.17 (2C), 52.89, 52.79, 52.28, 43.99, 33.95, 29.80, 29.28; IR (film, cm^{-1}): 3020, 2950, 1720, 1620, 1435, 1060, 950.

Endo-5-*exo*-17-Dicarbomethoxy-12,13-benzo-pentacyclo[7.4.3.0^{2,8}.0^{10,15}.0^{16,18}]- octadeca-2(8),3,6,12-tetraene-11,14-dione (19): Naphthoquinone (170 mg, 0.63 mmol) and ***cis*-2** (150 mg, 0.55 mmol) were dissolved in 10 mL $CHCl_3$. The solution was stirred at r.t. for 8 days. The solvent was evaporated and the residue purified by crystallization from ether giving the monoaddition product **19** (158 mg, 59%): pale-brown crystals, mp 166-167°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.94-7.26 (AA'BB' system, 4H), 5.80 (d, A part of AX system, J=8.7 Hz, 2H), 4.97 (dd, X part of AX system, J=8.7 Hz, J=5.5 Hz, 2H), 3.88 (m, 2H), 3.71 (s, OCH_3, 3H), 3.62 (s, OCH_3, 3H), 3.43 (bs, 2H), 2.22 (t, J=5.5 Hz, 1H), 1.94 (m, 2H), 1.02 (t, J=2.7 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 199.81, 173.31, 173.27, 137.48, 135.77, 134.64, 127.16, 126.45, 112.89, 52.61, 52.21, 50.46, 43.65, 42.20, 22.04, 18.75; IR (KBr, cm^{-1}) 3050, 3020, 2950, 1740, 1720, 1675, 1590, 1435, 1410, 1165, 1035, 1005, 925.

Exo-5-exo-17-Dicarbomethoxy-12,13-benzo-pentacyclo[7.4.3.$0^{2,8}$.$0^{10,15}$.$0^{16,18}$]octadeca-2(8),3,6,12-tetraene-11,14-dione (20): Naphthoquinone (100 mg, 0.37 mmol) and ***trans*-2** (100 mg, 0.37 mmol) were dissolved in 10 mL $CHCl_3$. The solution was stirred at r.t. for 9 days. The solvent was evaporated and the residue purified by crystallization from ether giving the monoaddition product **20** (115 mg, 70%): dark-brown crystals, mp 180-181°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.90-7.26 (AA'BB' system, 4H), 5.93 (d, A part of AX system, J=8.4 Hz, 2H), 4.90 (dd, X part of AX system, J=8.4 Hz, J=5.6 Hz, 2H), 3.70 (m, 2H), 3.64 (s, OCH_3, 3H), 3.63 (s, OCH_3, 3H), 3.38 (br.s, 2H), 2.05 (m, 2H), 0.95 (t, J=2.7 Hz, 1H), 0.50 (t, J=5.6 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 197.02, 173.42, 173.29, 137.49, 135.78, 134.71, 127.14, 125.74, 111.43, 52.49, 52.38, 49.89, 43.25, 41.72, 22.20, 18.39; IR (KBr, cm^{-1}) 3080, 3020, 3000, 2950, 1730, 1720, 1680, 1590, 1440, 1415, 1340, 1310, 1280, 1250, 1170, 1025, 1000, 930.

***syn*-25**: To a refluxing solution of **18** (210 mg, 0.5 mmol) in 40 ml of ethylene dichloride, benzenediazonium 2-carboxylate hydrochloride (650 mg, 3.5 mmol) was added. The colorless solution became dark. The reaction mixture was refluxed for 1 day and the solvent evaporated. The residue was filtered through silica gel (10 g) with $CHCl_3$ (200 mL) and the adduct ***syn*-25** purified by crystallization from $CHCl_3$/ether. ***syn*-25** was recrystallized from acetone/ether as colorless crystals (80 mg, 32%): mp 179-181°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.06-6.83 (AA'BB' system, 4H), 4.13 (m, 2H), 4.01 (m, 2H), 3.66 (s, OCH_3, 3H), 3.65 (s, OCH_3, 3H), 3.59 (s, OCH_3, 6H), 2.60 (t, J=2.8 Hz, 1H), 2.6 (t, J=2.9 Hz, 1H), 2.11 (m, 2H), 1.99 (m, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 172.39, 171.52, 166.37, 148.92, 147.71, 146.66, 125.25, 123.91, 52.44, 52.38, 52.29, 45.18, 44.96, 31.84, 30.61, 29.89, 29.45; IR (KBr, cm^{-1}) 3020, 2980, 2955, 1735, 1720, 1620, 1435, 1400, 1300, 1265, 1220, 1145, 1050, 915.

***syn*-25: 21** (414 mg, 1 mmol) [7] was reacted with benzenediazonium 2-carboxylate hydrochloride as described above. Colorless crystals (87 mg, 18%) from acetone/ether. Mp.: 224-226°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.24-7.06 (AA'BB' system, 4H), 4.22 (m, 2H), 4.11 (m, 2H), 3.84 (s, OCH_3, 6H), 3.57 (s, OCH_3, 3H), 3.38 (s, OCH_3, 3H), 1.96-1.88 (m, 4H), 1.06 (t, J=2.9 Hz, 1H), 0.08 (t, J=2.8 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 172.50, 171.36, 166.68, 147.58, 145.22, 140.53, 125.79, 124.09, 52.87, 52.12, 52.02, 44.38, 44.18, 312.12, 30.31, 28.09, 27.31.; IR (KBr, cm^{-1}) 3050, 2950, 1715, 1615, 1430, 1390, 1310, 1255, 1140, 1030, 910.

***syn*-26**: Dihydroheptalane derivative ***cis*-2** (100 mg, 0.37 mmol) and 1.5 g of dimethyl acetylenedicarboxylate were heated at 100±5°C in a sealed tube for 2 days. The reaction mixture was cooled to room temperature and 2 mL of ether was added. The ether solution was delayed for 1 day. The formed precipitate was recrystallized from ether to give bisadduct ***syn*-26** as white crystals (140 mg, 69%): mp 161-162°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.19 (m, 4H), 3.72 (s, OCH_3, 12H), 3.66 (s, OCH_3, 6H), 2.53 (t, J=2.8 Hz,2H), 2.16 (m, 4H);δ^{13}C-NMR (50 MHz, $CDCl_3$) δ 171.27, 166.24, 149.52, 148.78, 52.73, 52.45, 31.97, 30.51; IR (KBr, cm^{-1}) 3040, 3000, 2950, 1720, 1700, 1610, 1440, 1405, 1290, 1260, 1155, 1045, 925.

***anti*-26: *trans*-2** (100 mg, 0.37 mmol) and dimethylacetylene dicarboxylate (1.5) was reacted as described above. White crystals from $CHCl_3$/ether (145 mg, 71%); mp: 255-257°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.22 (m, 4H), 3.81 (s, OCH_3, 12H), 3.56 (s, OCH_3, 6H), 2.05 (m, 4H), 0.94 (t, J=2.8 Hz, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 171.36, 166.41, 147.55, 140.02, 52.93, 52.23, 32.89, 27.79; IR (KBr, cm^{-1}) 3050, 3000, 2950, 1720, 1620, 1435, 1395, 1270, 1145, 1050, 910; Anal Calcd for C28H28O12: C, 60.43; H, 5.07; Found: C, 60.59, H, 4.94.

27: **22** (150 mg, 0.41 mmol) [7] and dimethyl acetylenedicarboxylate (1 g) were reacted as described above. White crystals from $CHCl_3$/ether (120 mg, 58%); mp: 271-273°C. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.13 (m, 2H), 3.81 (s, OCH_3, 6H), 3.72 (m, 2H), 3.63 (s, OCH_3, 3H), 3.59 (s, OCH_3, 3H), 3.43 (m, 2H), 2.08 (m, 2H), 1.78 (t, J=2.8 Hz, 1H), 1.68 (m, 2H), 0.44 (t, J=2.9 Hz, 1H);δ^{13}C-NMR (50 MHz, $CDCl_3$) δ 172.23, 171.30, 171.21, 166.10, 146.08, 139.08, 53.03, 52.68, 52.63, 46.43, 44.42, 37.01, 30.93, 29.03, 22.74, 20.62; IR (KBr, cm^{-1}) 2950, 1775, 1735, 1710, 1440, 1315, 1260, 1230, 915; Anal Calcd for C26H24O11: C, 60.94; H, 4.72; Found: C, 60.44, H, 4.63.

28: **23** (50 mg, 0.11 mmol) [15] and dimethyl acetylenedicarboxylate (500 mg) were reacted as described above. White crystals from $CHCl_3$/ether (120 mg, 58%); mp: 237-239°C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.62-7.26 (m, 5H), 5.39 (m, 2H), 4.37 (m, 2H), 3.84 (s, OCH_3, 6H), 3.62 (s, OCH_3, 3H), 3.52 (s, OCH_3, 3H), 2.19 (m, 4H), 1.40 (t, J=2.8 Hz, 1H), 0.58 (t, J=3.0 Hz, 1H);δ^{13}C-NMR (50 MHz, $CDCl_3$) δ 171.01, 170.58, 165.71, 154.67, 146.97, 136.81, 132.02, 129.39, 126.65, 125.68, 54.99, 53.08, 52.75, 52.18, 43.19, 32.12, 27.95, 22.37, 15.09; IR (KBr, cm^{-1}) 3050, 3000, 2950, 1715, 1435, 1410, 1300, 1260, 920. Anal Calcd for C30H27O10N3: C, 61.12; H, 4.62, N,7.13; Found: C, 61.02, H, 4.91, N, 6.95.

30: Monocycloadduct **20** (210 mg, 0.11 mmol) and dimethyl acetylenedicarboxylate (1.5 g) were reacted as described above. Yellow powder (95 mg, 34%) from $CHCl_3$/ether; mp: 254-256°C; ^{1}H-NMR. (200 MHz, $CDCl_3$) δ 8.15-7.73 (AA'BB' system, 4H), 4.75 (m, 2H), 4.27 (m, 2H), 3.84 (s, OCH_3, 6H), 3.57 (s, OCH_3, 3H), 3.34 (s, OCH_3, 3H), 2.04 (m, cyclopropane, 2H), 1.98 (m, 2H), 1.09 (t, J=2.8 Hz, 1H), 0.55 (t, J=2.8 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 181.66, 171.43, 170.75, 166.36, 155.26, 147.58, 140.06, 134.31, 132.36, 127.08, 53.01, 52.39, 52.08, 44.07, 39.20, 33.21, 32.78, 28.00, 27.67; IR (KBr, cm^{-1}) 3040, 3000, 2940, 1720, 1655, 1590, 1430, 1390, 1280, 1150, 1050, 1010, 1020, 990; Anal Calcd for C32H26O10: C, 67.37; H, 4.59; Found: C, 67.41, H, 4.25.

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