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Characterization of [*n*]-Ladderanes of Unprecedented Length: A New Record for Fused Carbocyclic Arrays[†]

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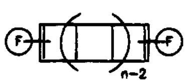
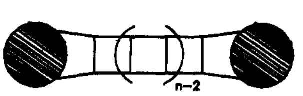
Summary: Characterization of [9]-, [11]-, and [13]-ladderanes of record length and nanometric dimension, obtained in the oligomerization of 1,2-dicarbomethoxycyclobutadiene, is described.

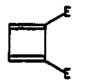
We have recently shown that just as squares serve as versatile building blocks for shapes in art and architecture, an appropriately substituted cyclobutadiene is an effective molecular module for the rapid assembling of linearly fused and doubly end-functionalized polyquadranoid frameworks.[1] The resulting functionalized [*n*]-ladderanes **1** have the promising potential to function as rigid rods, spacers, and connectors, e.g., **2**,for designing new materials and molecular level devices.[2] In **2**, the shaded circles could be diverse donor−acceptor groups, polar heads, or even fullerenes. To augment and evaluate such capabilities, it is desirable to have access to ladderanes of nanometric dimension.[3] Also, higher [*n*]-ladderanes through end-to-end cyclization, fragmentation, and rearrangement protocols can be the harbingers of some novel carbocyclic architecture.[1,4]



1



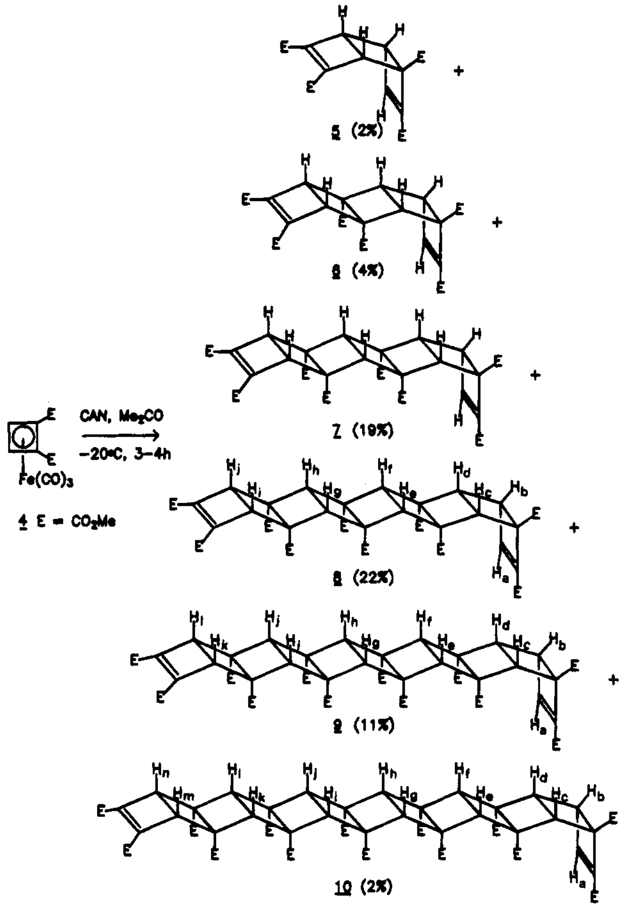
2



3 E = CO_2Me

In an earlier report from our laboratory, it has been demonstrated that FMO controlled regio- and stereoselective oligomerization of 1,2-dicarbomethoxycyclobutadiene (**3**) released from the complex **4**[5] furnished [3]- (**5**), [5]- (**6**), and [7]-ladderane (**7**) (3:2:1) in 55% yield.[1] We have now observed that through subtle variation of concentration and temperature, a dramatic alteration in the oligomerization profile of **3** can be effected and a panorama of [*n*]-ladderanes unfolds, Scheme 1. Herein, we report the characterization of [9]-, [11]-, and [13]-ladderanes of record length (≈1−1.6 nm). To our knowledge, no carbocyclic system embodying as many as 13 fused rings, identical or mixed, is known in the literature.[6] In addition, we delineate an "end-correction" sequence that eventuates in the formation of heretofore unknown, even numbered, symmetrical *all-exo*-[6]- and [8]-ladderanes.[3]

Scheme 1



Stirring a thick slurry of **4** (0.8 mmol) and ceric(IV) ammonium nitrate in minimal amount of dry acetone (1−2 mL) at −20 °C for 3−4 h, followed by usual workup and repeated chromatography on silica gel, led to the isolation of six odd-membered ladderanes **5−10** in ≈60% yield, Scheme 1.[7] While [3]- (**5**), [5]- (**6**), and [7]-ladder-

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[†] Dedicated to the memory of Prof. Paul G. Gassman.

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(1) Mehta, G.; Viswanath, M. B.; Sastry, G. N.; Jemmis, E. D.; Reddy, D. S. K.; Kunwar, A. C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1488. See also: Overberger, C. G.; Moore, J. A. *Adv. Polymer Aci.* **1970**, *7*, 113−150.

(2) (a) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, V. *J. Am. Chem. Soc.* **1993**, *115*, 4919. (b) Lawson, J. M.; Paddon-Row, M. N. *J. Chem. Soc., Chem. Commun.* **1993**, 1641 and earlier papers from this group. (c) Mathias, J. P.; Stoddart, J. F. *Chem. Soc. Rev.* **1992**, *21*, 215 and references cited therein.

(3) Molecular mechanics calculations (MM2: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8122) on unsubstituted [*n*]-ladderanes indicated that end-to-end distance in [8]-ladderanes (fully stretched zig−zag form) is ≈1 nm and ladderanes beyond it can be regarded as having a nanometric dimension. To date, only [3]-, [4]-, [5]-, and [7]-ladderanes are described in the literature; see also ref 1.

(4) (a) Dinsburg, G. *Nouv. J. Chem.* **1982**, *6*, 175. (b) Mehta, G.; Viswanath, M. B.; Ravi Kumar, K.; Kunwar, A. C.; Reddy, D. S. K. *J. Chem. Soc., Chem. Commun.* **1994**, 739.

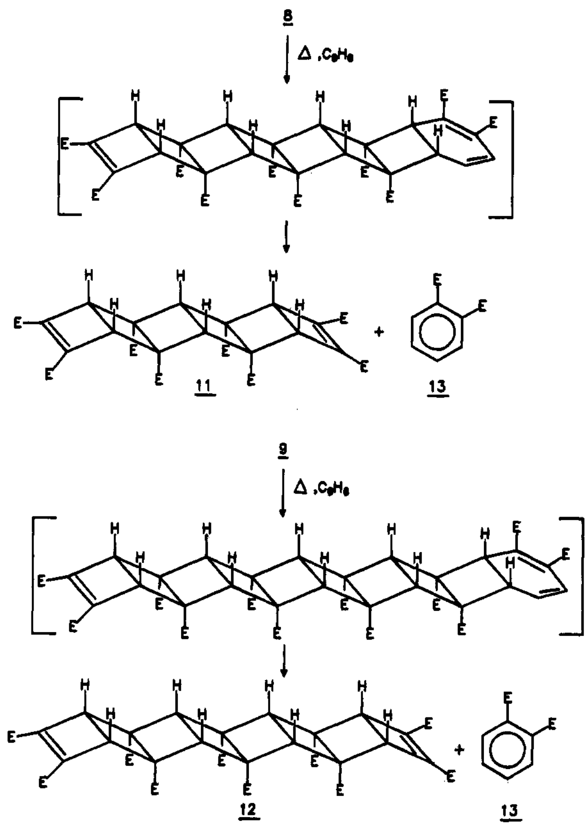
(5) Berens, G.; Kaplan, F.; Rimerman, R.; Roberts, B. W.; Wissner, A. *J. Am. Chem. Soc.* **1975**, *97*, 7076.

(6) A close example that comes to mind could be of polyacenes with up to 19 fused rings, but they are interspersed with aromatic rings and are curved.[2c] See also: Thomas, A. D.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4160.

(7) In the present study, Ce^{4+} decomposition of **4** has been carried out at lower temperature (−20 °C, cf. 0−5 °C earlier[1]) and at higher concentration (slurry form). Thus, there is slow release of monomer **3**, and its effective concentration is maintained, which promotes oligomerization. Also, it is well known that at higher concentration, formation of higher oligomers is favored.

0022-3263/94/1959-6131$04.50/0

Scheme 2



ane (**7**) were readily recognized through comparison with earlier samples, the structures of [9]-, (**8**),[9] [11]- (**9**),[9] and [13]-ladderane (**10**)[9] were elucidated on the basis of expected chemical shifts (cf. **5**–**7**), selective decoupling data, NOE and NOSEY experiments, and FAB-MS. The high field ^{1}H and ^{13}C NMR parameters were decisive and indicated the presence of 10, 12, and 14 methyl ester moieties in **8**, **9**, and **10**, respectively. The regio- and stereostructures of **8**–**10** followed from the pattern of **5**–**7** and are fully in agreement with the predictions based on our calculations[1] and the spectral data.

While we were elated at being able to erect a "long ladder", e.g., **10**, we were concerned at the fact that the initial dimerization of **3** leads to the unsymmetrical, folded, and less desirable dimer **5**. This "fold" is an irksome feature that perpetuates as the ladder grows during oligomerization. We, therefore, sought to mitigate this limitation by sacrificing the cyclobutane rings of the fold, at the unsymmetrical termini, to generate shorter but perfect ladders. Thermal activation (C_6H_6, Δ, 24 h) of [9]-ladderane (**8**) and [11]-ladderane (**9**) led to the isolation of [6]-ladderane (**11**)[9] and [8]-ladderane (**12**),[9] respectively, along with some dimethyl phthalate (**13**) and minor impurities in ≈50% yield, Scheme 2. The remarkably simple ^{1}H NMR spectra of **11** (four lines, 1:2: 6:6) and **12** (five lines, 2:2:3:6:6) along with diagnostic ^{13}C NMR data secured their formulation. The notable feature of the thermolyses of **8** and **9** is the regioselective cyclobutene ring opening at the unsymmetrically substituted end followed by fragmentation[8] to furnish symmetrical, even-membered (*exo,exo*) [6]- (**11**) and [8]-ladderane (**12**), Scheme 2.[3]

In summary, we have delineated an extremely simple access to both even- and odd-numbered [*n*]-ladderanes (up to *n* = 13), resembling "molecular waves" and of unprecedented length. Availability of symmetrical, doubly end-functionalized, and dipolarofacial molecular connectors of flexible length like **11** and **12**, in addition to **8**–**10**, augurs well for further exploration of their utility.

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Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra of **8**–**12** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[8] For related examples see: Warrener, R. N.; Wang, J. M.; Weerasuia, K. D. V.; Russell, R. A. *Tetrahedron Lett.* **1990**, *31*, 7069.

[9] ^{1}H and ^{13}C NMR data for ladderanes **8**–**12**. **8**: mp 155–156 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.89 (d, J_{ab} = 1.1 Hz, 1H, H$_a$), 3.81 (s, 3H, COOMe), 3.75 (s, 3H, COOMe), 3.74 (d, J_{cd} = 5.8 Hz, 1H, H$_c$), 3.72 (s, 3H, COOMe), 3.69 (s, 3H, COOMe), 3.69 (s, 3H, COOMe), 3.69 (dd, J_{bd} = 8.5 Hz, J_{ab} = 1.1 Hz, 1H, H$_b$), 3.60 (d, J_{ij} = 2.4 Hz, 1H, H$_i$), 3.57 (s, 3H, COOMe), 3.56 (s, 3H, COOMe), 3.56 (s, 3H, COOMe), 3.54 (d, J_{ij} = 2.4 Hz, 1H, H$_j$), 3.53 (s, 3H, COOMe), 3.47 (s, 3H, COOMe), 3.31 (d, J_{ef} = 3.7 Hz, 1H, H$_e$), 3.22 (d, J_{gh} = 3.8 Hz, 1H, H$_h$), 3.19 (d, J_{gh} = 3.8 Hz, 1H, H$_g$), 3.18 (d, J_{ef} = 3.7 Hz, 1H, H$_f$), 3.17 (dd, J_{bd} = 8.5 Hz, J_{cd} = 5.8 Hz, 1H, H$_d$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.6, 169.0, 168.0, 167.9, 167.7, 167.5, 167.4, 160.7, 160.7, 160.3, 147.2, 144.3, 141.2, 139.8, 57.1, 55.6, 55.4, 54.6, 54.5, 54.4, 54.4, 53.2, 52.4, 52.1, 52.1(2C), 51.7, 51.4, 51.3, 51.2, 51.2, 51.0, 50.8(2C), 50.6, 46.7, 46.5, 46.2, 43.7, 42.5; FAB-MS [M + H]$^+$ 841, [M + Na]$^+$ 863. **9**: mp 177–178 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.88 (d, J_{ab} = 1.1 Hz, 1H, H$_a$), 3.84 (s, 3H, COOMe), 3.74 (s, 3H, COOMe), 3.73 (d, J_{cd} = 5.8 Hz, 1H, H$_c$), 3.71 (s, 3H, COOMe), 3.69 (s, 3H, COOMe), 3.69 (s, 3H, COOMe), 3.68 (dd, J_{ab} = 1.1 Hz, J_{bd} = 8.5 Hz, 1H, H$_b$), 3.60 (s, 3H, COOMe), 3.60 (d, J_{kl} = 2.4 Hz, 1H, H$_k$), 3.58 (s, 3H, COOMe), 3.57 (s, 3H, COOMe), 3.54 (s, 3H, COOMe), 3.54 (d, J_{kl} = 2.4 Hz, 1H, H$_1$), 3.53 (s, 3H, COOMe), 3.52 (s, 3H, COOMe), 3.44 (s, 3H, COOMe), 3.30 (d, J_{ef} = 3.6 Hz, 1H, H$_e$), 3.25 (d, J_{ij} = 3.8 Hz, 1H, H$_j$), 3.24 (d, J_{gh} = 3.8 Hz, 1H, H$_g$), 3.22 (d, J_{gh} = 3.8 Hz, 1H, H$_h$), 3.17 (d, J_{ef} = 3.6 Hz, 1H, H$_f$), 3.16 (dd, J_{bd} = 8.5 Hz, J_{cd} = 5.8 Hz, 1H, H$_d$), 3.16 (d, J_{ij} = 3.8 Hz, 1H, H$_i$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.6, 168.8; 168.2, 167.9, 167.6, 167.5, 167.4, 167.2, 166.9, 161.0, 160.7, 160.4, 147.2, 144.8, 140.6, 139.9, 56.8, 55.4, 55.3, 54.8, 54.7, 54.5, 54.4, 54.3, 54.0, 53.4, 53.0, 52.7, 52.4, 52.2, 52.2, 52.1, 51.8, 51.4, 51.3, 51.2, 51.1, 51.0, 50.8 (2C), 50.7, 50.7, 50.5, 46.3 (2C), 46.2, 43.8, 42.7; FAB-MS [M + H]$^+$ 1009 [M + Na]$^+$ 1031. **10**: mp 181–182 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.87 (d, J_{ab} = 1.1 Hz, 1H, H$_a$), 3.83 (s, 3H, COOMe), 3.74 (s, 3H, COOMe), 3.73 (d, J_{cd} = 5.7 Hz, 1H, H$_c$), 3.71 (s, 3H, COOMe), 3.69 (s, 3H, COOMe), 3.68 (s, 3H, COOMe), 3.67 (dd, J_{ab} = 1.1 Hz, J_{bd} = 8.5 Hz, 1H, H$_b$), 3.64 (d, J_{mn} = 2.3 Hz, 1H, H$_m$), 3.60 (s, 3H, COOMe), 3.59 (s, 3H, COOMe), 3.57 (s, 3H, COOMe), 3.56 (s, 3H, COOMe), 3.56 (s, 3H, COOMe), 3.55 (s, 3H, COOMe), 3.55 (d, J_{mn} = 2.3 Hz, 1H, H$_n$), 3.53 (s, 3H, COOMe), 3.51 (s, 3H, COOMe), 3.43 (s, 3H, COOMe), 3.30 (d, J_{ef} = 3.6 Hz, 1H, H$_e$), 3.26 (d, J_{kl} = 3.8 Hz, 1H, H$_1$), 3.25 (d, J = 3.7 Hz, 1H), 3.23 (d, J = 3.7 Hz, 1H), 3.21 (d, J = 3.7 Hz, 1H), 3.20 (d, J = 3.7 Hz, 1H), 3.17 (d, J_{ef} = 3.6 Hz, 1H, H$_f$), 3.16 (d, J_{kl} = 3.8 Hz, 1H, H$_k$), 3.16 (dd, J_{bd} = 8.5 Hz, J_{cd} = 5.7 Hz, 1H, H$_d$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.6, 168.8, 168.0, 167.9, 167.4, 167.4, 167.4, 167.3(2C), 167.1, 166.9, 160.9, 160.7, 160.4, 147.2, 144.8, 140.7, 139.9, 56.8, 55.4, 55.1, 54.8, 54.7, 54.4, 54.4, 54.2, 54.2, 54.1, 53.9, 53.4, 52.9, 52.9, 52.8, 52.8, 52.4, 52.3, 52.1, 52.1, 51.8, 51.5, 51.3, 51.1, 51.1, 51.0, 50.8, 50.8, 50.8, 50.7, 50.7, 50.6, 50.4, 46.4, 46.2, 46.2, 43.7, 42.6. **11**: mp 216–217 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.81 (s, 12H), 3.61 (s, 4H), 3.55 (s, 12H), 3.24 (s, 2H); ^{13}C NMR (50.0 MHz, CDCl$_3$) δ 167.9, 160.9, 142.9, 56.8, 52.2, 51.3, 49.0, 46.3; FAB-MS [M + H]$^+$ 647 [M + Na]$^+$ 669. **12**: mp 238–239 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.80 (s, 12H), 3.60 (s, 4H), 3.57 (s, 12H), 3.55 (s, 6H), 3.25 (s, 4H); ^{13}C NMR (50.0 MHz, CDCl$_3$) δ 167.9, 160.8, 142.8, 56.1, 55.1, 52.2, 51.4, 50.9, 46.4; FAB-MS [M + H]$^+$ 815 [M + Na]$^+$ 837.