Oligo(cyclohexylidenes): Parent Compounds and End-Functionalized Derivatives

Frans J. Hoogesteger,† Remco W. A. Havenith,† Jan W. Zwikker,† Leonardus W. Jenneskens,*,† Huub Kooijman,‡ Nora Veldman,‡ and Anthony L. Spek‡

Debye Institute, Department of Physical Organic Chemistry, and Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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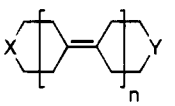
Parent oligo(cyclohexylidenes) **1(*n*)** (***n*** = 1–4) were synthesized using a modified Barton–Kellogg olefin synthesis. Surprisingly, the crude compounds **1(2)** and **1(4)** contained small amounts of the **1(*n*−1)** and **1(*n*+1)** homologues. As evidenced by a close examination of mass spectral data of selectively deuterated tercyclohexylidenes **1(2)-d_4d_4** and **1(2)-d_8**, their formation can be attributed to scrambling of the intermediate azines. With increasing ***n***, a marked decrease in solubility as well as an increase in thermal stability was found. Powder diffraction measurements indicate that the parent compounds **1(*n*)**, irrespective of ***n***, pack in a similar fashion in the solid state. The theoretically (MMX, AM1, and *ab initio*) predicted rodlike structure of the oligo(cyclohexylidenes) was confirmed by single-crystal X-ray structures of **1(1)** and three derivatives (**12(1)**, **13(1)**, and **30(2)**). In line with the powder diffraction data in the series **1(*n*)**, a similar packing motif was found for the derivatives. To circumvent side product formation due to azine scrambling, a different synthetic approach was used for the preparation of end-functionalized oligo(cyclohexylidenes), *i.e.* decarboxylation and dehydration of β-hydroxy acids.

Introduction

The design, synthesis, and characterization of (functionalized) rodlike molecular building blocks for supramolecular assemblies receives considerable attention[1,2] due to their potential application as optoelectric, conductive, or new structural materials.

Early examples of rodlike compounds derived from alicyclics are oligomers consisting of bicyclo[2.2.2]octyl units which were used for electron and energy transfer studies.[3] More recently, [*n*]staffanes, consisting of up to five covalently linked bicyclo[1.1.1]pentane units,[4a–c] which can be end-functionalized with a variety of substituents[4d–e] have been prepared. Properties studied include the formation of Langmuir–Blodgett films,[4f] self-assembled monolayers (SAM's),[4g] and the occurrence of through-bond long-range spin density propagation.[4h] Other hydrocarbons also possessing a rodlike structure include [*n*]ladderanes,[5] oligo(cubanes),[6] oligo-*p*-carboranes,[7] oligo-*p*-phenylenes,[8] and oligocarbynes.[9] Note, however, that, in most cases, the rod-type molecules are prepared as oligomeric mixtures; albeit, extensive purification is required for the isolation of the pure oligomers.

In this context, we were prompted to investigate oligo(cyclohexylidenes) **1(*n*)**. These oligomers consist of cyclohexyl groups linked together at the 1,4-positions *via* exocyclic double bonds. Molecular Mechanics (MMX), semiempirical (AM1), and *ab initio* (6-31G basis set) calculations[10] predict that they possess a regular, elongated structure with the cyclohexane-type rings in a chairlike geometry, suggesting that these molecules are potential candidates for the design of ordered molecular assemblies. Furthermore, the alternating σ–π–σ orbital topology makes them interesting for application as redox active bridges in donor–bridge–acceptor-type compounds giving access to new optoelectric materials.[11]



Hitherto, bicyclohexylidene **1(1)** and some of its 4,4′-substituted derivatives have been synthesized by various methods,[12] of which the Barton–Kellogg olefin synthesis is most common.[13] Longer oligo(cyclohexylidenes) up to ***n*** = 3 containing carbonyl functionalities at both end

† Debye Institute.
‡ Bijvoet Center for Biomolecular Research.
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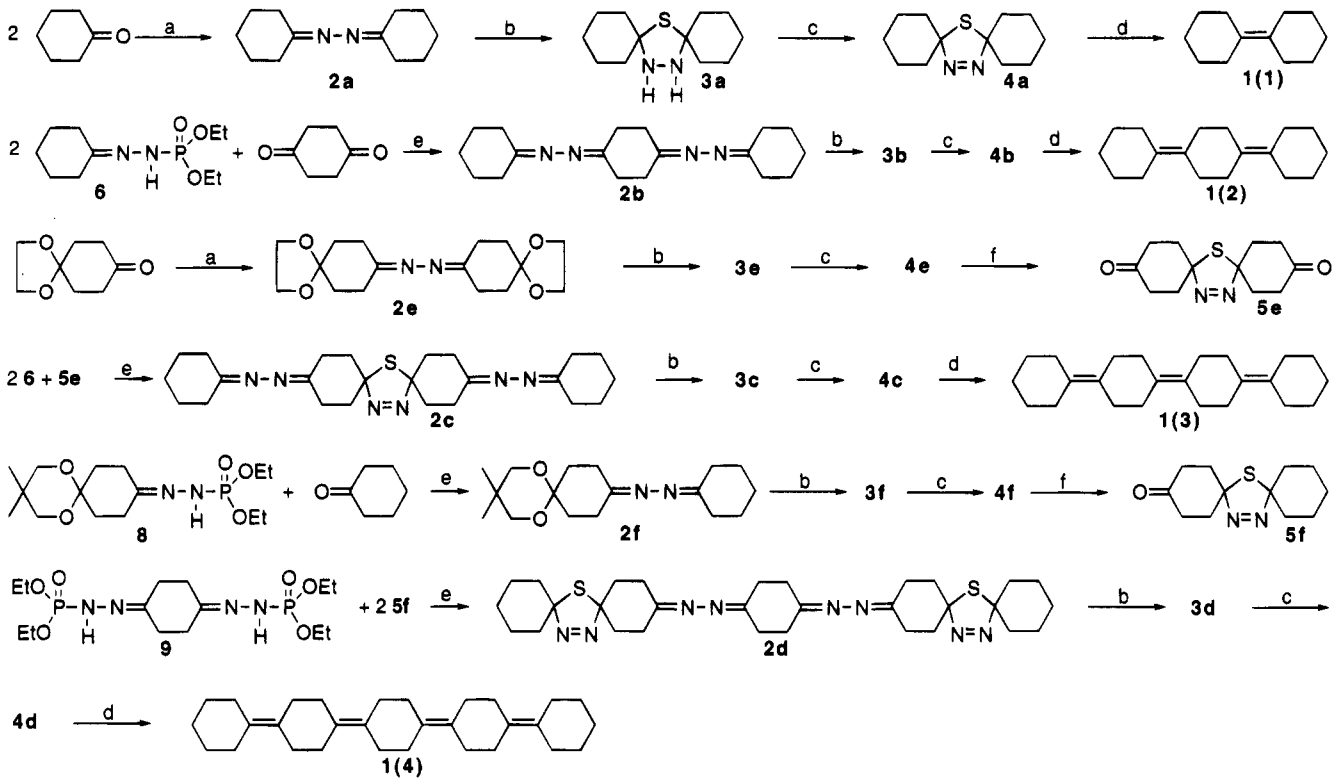
Scheme 1. Synthetic Scheme for Parent Oligo(cyclohexylidenes) 1(*n*)[a]



[a] (a) H_2NNH_2, EtOH; (b) H_2S, CH_3CN/CH_2Cl_2; (c) $Pb(OAc)_4$, $CaCO_3$, CH_2Cl_2; (d) ΔT, $P(OEt)_3$, toluene; (e) NaH, THF; (f) H_3O^+, CH_2Cl_2.

positions have been reported as intermediates in the synthesis of macrocyclic compounds,[14] and in the parent series, compound **1(2)** has been observed as a byproduct.[14c]

Here we report on the synthesis and properties of parent oligo(cyclohexylidenes) **1(*n*)** (X = Y = CH_2) and a series of end-functionalized (X and/or Y ≠ CH_2) derivatives. Their accessibility holds a promise for the preparation of supramolecular structures using the Langmuir–Blodgett technique, self-assembly, and directional hydrogen bonding as well as for the study of $\pi-\sigma-\pi$ interactions.

Results and Discussion

Parent Compounds 1(*n*). Oligo(cyclohexylidenes) **1(*n*)** were prepared according to Scheme 1. The synthetic pathway is based on the 2-fold extrusion methodology developed by Barton and Kellogg.[13] An azine **2** is converted into a thiadiazolidine **3** by treatment with hydrogen sulfide followed by oxidation to the related thiadiazoline **4**. Finally, consecutive extrusion of nitrogen and desulfurization using triethyl phosphite gives the desired oligo(cyclohexylidene) **1(*n*)**. The required azines for oligomers with ***n*** > 1 were obtained using a Horner–Emmons reaction of a hydrazone and an appropriate ketone.[14c,15] Quinquecyclohexylidene **1(4)** was synthesized from azine precursor **2d**, obtained from ketone **5f** and bishydrazone **9**.

Table 1. Yields and Thermal Properties of Oligo(cyclohexylidenes) 1(*n*)

n	yield (%)[a]	T_m (°C)[b]	T_{onset} (°C)[c]	T_{max} (°C)[d]
1	76	55.6	60[e]	–
2	33	161.7	130[e]	–
3	38	200 dec	200	308
4[f]	22	249 dec	230	370

[a] Yield based on azines **2a**, **2b**, **2c**, and **2d**, respectively. [b] Melting point determined using DSC (peak maximum). [c] TGA (N_2); onset temperature for thermal decomposition. [d] TGA (N_2); temperature of maximum decomposition derived from first derivative TGA curve. [e] Sublimation of the compound. [f] Purity *ca.* 80%; impurities were identified as **1(3)** and **1(5)** (see text).

Oligo(cyclohexylidenes) **1(*n*)** were isolated as white, crystalline solids in overall yields ranging from 76% for bicyclohexylidene **1(1)** to 22% for quinquecyclohexylidene **1(4)** (Table 1). However, as evidenced by GC/MS analyses, purification of the crude oligo(cyclohexylidenes) **1(*n*)** with ***n*** = 2 and 4 was necessary; *i.e.* the crude product **1(*n*)** was contaminated with both the lower (**1(*n*−1)**) and higher (**1(*n*+1)**) homologue. The amount of these side products varied from 5% (***n*** = 2) to 20% (***n*** = 4). The side products could be removed by either recrystallization or sublimation of the crude product mixture except in the case of **1(4)**, due to the similar properties of the side

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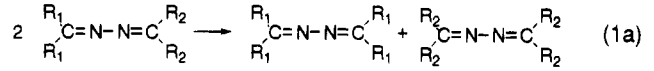
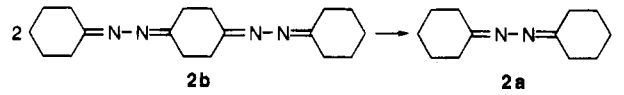
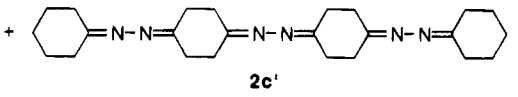
products and the main compound. Compound **1(4)** was obtained in a purity of *ca.* 80%, the only impurities being quatercyclohexylidene **1(3)** and sexicyclohexylidene **1(5)** (*vide infra*).

Azine Scrambling. The formation of side products **1(*n*−1)** and **1(*n*+1)** during the synthesis of **1(*n*)** with ***n*** = 2 and 4 is unexpected if one examines the synthetic pathway (Scheme 1). Formally, formation of azine **2** determines the number of cyclohexyl units in the oligomer. Note that neither the conversion of azine **2** to thiadiazolidine **3** and subsequent oxidation to thiadiazoline **4** nor the desulfurization to the oligo(cyclohexylidene) **1(*n*)** is expected to give rise to a change in the number of cyclohexyl groups in the oligomer. As evidenced by NMR spectroscopy, azines **2** were pure compounds. Nevertheless, it has been reported that scrambling of asymmetrically substituted azines to the corresponding symmetrical azines takes place (eq 1a).[12f,16]



(1a)

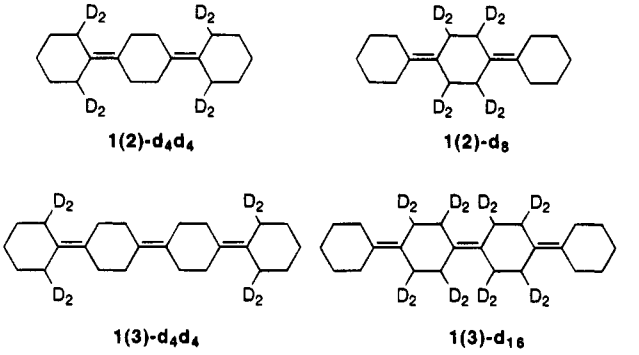




(1b)

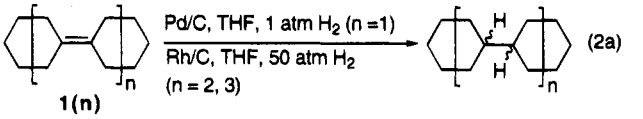
Although the mechanism is not fully resolved, it has been observed that the disproportionation of asymmetrical azines can be affected by air, traces of moisture, acid, and elevated temperatures. The rearrangement has been attributed to an asymmetrical charge distribution in the C=N−N=C linkage, which leads to a weakening of the N−N central bond and subsequently to the formation of free radicals from which stable symmetrical azines are formed.[16a] Although the azines **2b−d** are symmetrical molecules, every azine moiety is intrinsically asymmetrical, and thus, as an example, scrambling of azine **2b** would yield both **2a** and **2c'** (eq 1b). From the structure of precursor azine **2d**, it can be rationalized that oligo(cyclohexylidene) **1(4)** will be contaminated with **1(3)** and **1(5)**. The lack of side products in the case of **1(3)** is at present not well-understood. From the structure of azine **2c**, it is anticipated that, during the synthesis of **1(3)**, some **1(1)** and **1(5)** will be formed. Side products due to azine scrambling were also encountered during the synthesis of end-functionalized oligo(cyclohexylidenes) (*vide infra*).

Strong support for the occurrence of a scrambling process was derived from close scrunity of the reaction products obtained from the synthesis of selectively deuterated tercyclohexylidenes **1(2)-d_4d_4** and **1(2)-d_8**, in which the allylic positions of either the outer cyclohexyl-type rings or those of the central ring are deuterated. It is expected that quatercyclohexylidene side products resulting from scrambling of the precursor azines **2b-d_4d_4** and **2b-d_8** will differ with respect to the position and number of incorporated deuterium atoms. As shown by the GC/MS spectra of **1(2)-d_4d_4** and **1(2)-d_8**, this is indeed the case. Both compounds contain a trace amount of a partially deuterated quatercyclohexylidene. In the case of **1(2)-d_4d_4**, a side product at *m/e* 330 is found, while in the case of **1(2)-d_8**, the sole side product has *m/e* 340. This can be accounted for by equation 1b; quatercyclohexylidene **1(3)-d_4d_4** ($M^{+\cdot}$ *m/e* 332) with deuterated allylic positions in both outer rings is expected as a scrambling product during the synthesis of **1(2)-d_4d_4**, while in the case of **1(2)-d_8**, quatercyclohexylidene **1(3)-d_{16}** ($M^{+\cdot}$ *m/e* 340) with both central rings perdeuterated is expected. The molecular ion for **1(3)-d_4d_4** at *m/e* 330 can be rationalized by the fact that the starting [2,2,6,6-$^2H_4$]-cyclohexanone was only 37% d_4 (see the Experimental Section).

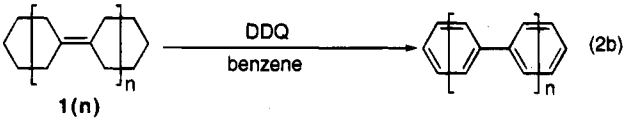


Properties of Oligo(cyclohexylidenes) 1(*n*). Compounds **1(*n*)** are stable to air and common organic solvents. Noteworthy is the marked decrease in solubility in common organic solvents (*n*-hexane, cyclohexane, diethyl ether, chloroform, toluene) with increasing ***n***. In keeping with the poor solubility, a significant increase in melting point (differential scanning calorimetry (DSC), T_m) and thermal stability (thermogravimetry (TGA) (N_2)) concomitant with increasing ***n*** was observed (Table 1). No evidence for liquid crystalline behavior was found (DSC and polarization microscopy).

Oligo(cyclohexylidenes) **1(*n*)** were readily converted into the saturated analogues by catalytic hydrogenation. In the case of ***n*** > 1, mixtures of *cis/trans* isomers were obtained (eq 2a). Furthermore, since compounds **1(*n*)** are



(2a)



(2b)

also precursors for oligo-*p*-phenylenes, oxidation using excess 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in refluxing benzene gave the corresponding oligo-*p*-phenylenes in good yields (eq 2b).

Spectroscopy of Compounds 1(*n*). Oligo(cyclohexylidenes) **1(*n*)** were characterized using ^1H and ^{13}C NMR (except quinquecyclohexylidene **1(4)** due to its insolubility), infrared spectroscopy, and mass spectroscopy.

The ^1H and ^{13}C NMR spectra of tercyclohexylidene **1(2)** were unequivocally assigned by comparison with the ^1H, ^2H, and ^{13}C NMR spectra of selectively deuterated compounds **1(2)-d_4d_4** and **1(2)-d_8**. The ^1H NMR spectrum of **1(2)** consists of a singlet at 2.26 ppm (8 H) and two multiplets at 2.18 (8 H) and 1.54 ppm (12 H),

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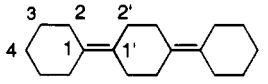
Table 2. ^{1}H and ^{13}C NMR Chemical Shifts of Tercyclohexylidene 1(2)[a]

^{1}H NMR		^{13}C NMR	
δ (ppm)	H atom no.	δ (ppm)	C atom no.
2.26	$2'_{ax}$; $2'_{eq}$	130.15	1
2.18	2_{ax}; 2_{eq}	128.03	1′
1.54	3_{ax}; 3_{eq}	30.13	2
	4_{ax}; 4_{eq}	29.38	2′
		28.46	3
		27.19	4

[a] Solvent, $CDCl_3$; 298 K.

respectively. The former multiplet is almost absent in the ^{1}H NMR spectrum of **1(2)-d_4d_4**, while that at 1.54 ppm has changed shape. This shows that the eight allylic protons of the two outer rings in **1(2)** resonate at 2.18 ppm, which is confirmed by the ^{2}H NMR spectrum of **1(2)-d_4d_4** (^{2}H δ 2.15 ppm). The ^{1}H NMR spectrum of **1(2)-d_8** lacks the singlet at 2.26 ppm, while the multiplets at 2.18 and 1.54 ppm remain unchanged. Hence, the singlet at 2.26 ppm is assigned to the eight allylic protons of the central ring. Indeed, the ^{2}H NMR spectrum of **1(2)-d_8** shows a single resonance at 2.23 ppm (Table 2). It should be noted that the axial and equatorial hydrogen atoms are isochronous at room temperature, indicating rapid ring interconversions on the NMR time scale; similar phenomena are observed for **1(1)** and **1(3)**.

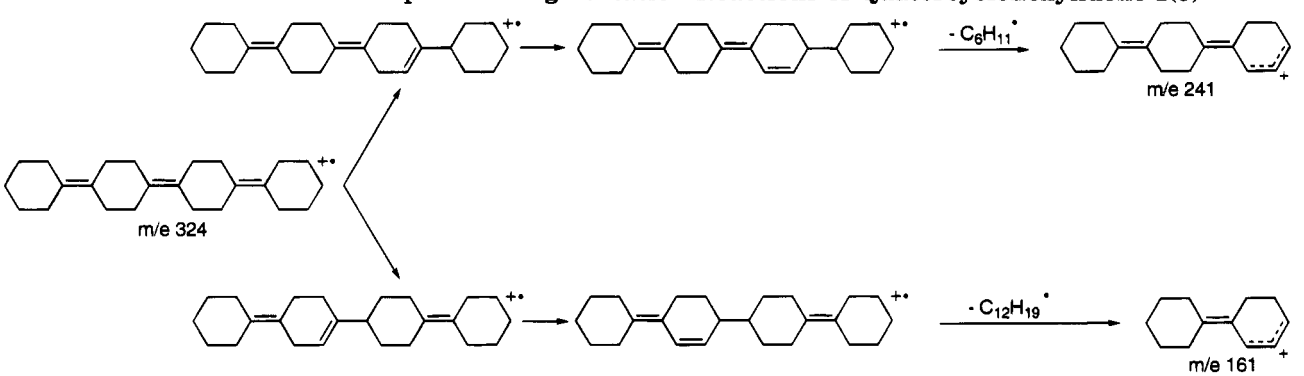
The ^{13}C NMR spectrum of **1(2)** shows two signals in the olefinic region (130.15 and 128.03 ppm) and four signals in the aliphatic region (30.13, 29.38, 28.46, and 27.19 ppm). The signal at 27.19 ppm possesses half the intensity of the other aliphatic resonances, indicating that it has to be assigned to the two terminal carbon atoms. In the ^{13}C NMR spectrum of **1(2)-d_4d_4**, the signal at 30.13 ppm is absent, while the intensity of the signal at 130.15 ppm is significantly reduced with respect to that at 128.03 ppm. The ^{13}C NMR spectrum of **1(2)-d_8** lacks the signal at 29.38 ppm, while the olefinic signal at 130.15 ppm is higher in intensity than the one at 128.03 ppm (Table 2).



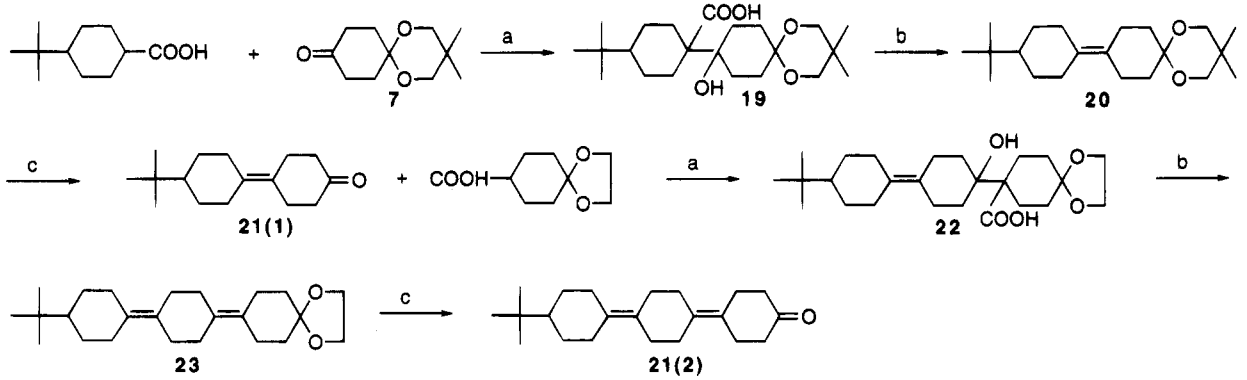
Diffuse reflectance FT-IR spectra of compounds **1(*n*)** (*n* > 1) are nearly identical. As confirmed by *ab initio* calculations,[17] this indicates that the longer oligomers belong to the same point group (C_{2h}). Strong bands are found between 2977 and 2851 cm^{-1} (CH stretch vibrations) and between 1446 and 1431 cm^{-1} (CH-bending vibrations). Apart from the above-mentioned CH stretch and CH-bending vibrations, the infrared spectra of tercyclohexylidenes **1(2)-d_4d_4** and **1(2)-d_8** show medium intensity bands between 2217 and 2076 cm^{-1} due to CD stretch vibrations (see the Experimental Section).

Mass spectrometry reveals that oligo(cyclohexylidenes) **1(*n*)** possess similar fragmentation patterns, irrespective of the value of *n*. The most intense mass peaks are found at *m/e* 244 (51% relative intensity, M$^{\bullet-}$) and 161 (100% relative intensity, M − 83) for **1(2)**, at *m/e* 324 (100% relative intensity, M$^{\bullet+}$), 241 (30% relative intensity, M − 83), and 161 (55% relative intensity, M − 163) for **1(3)**, and at *m/e* 404 (100% relative intensity, M$^{\bullet-}$), 321 (15% relative intensity, M − 83), 241 (21% relative intensity, M − 163), and 161 (39% relative intensity, M − 243) for **1(4)**. This suggests that two allylic hydrogen shifts occur in the radical cation before fragmentation. The species thus formed cleaves into an allylic-type cation and a cyclohexyl radical. In the case of longer oligo(cyclohexylidenes), bicyclohexylidene and tercyclohexylidene radicals are also expelled. As an illustration, the main rearrangement and fragmentation reactions for the radical cation of **1(3)** are shown in Scheme 2. This type of rearrangement prior to fragmentation is identical to that found for related compounds isopropylidenecyclohexane and $\Delta^{4(8)}$menthene.[19] Our interpretation is corroborated by the fragmentation patterns of the deuterated compounds **1(2)-d_8**, **1(3)-d_{16}**, **1(2)-d_4d_4**, and **1(3)-d_4d_4**. In the case of **1(2)-d_8**, the molecular ion is found at *m/e* 252 (100% relative intensity) and the main fragmentation peak at *m/e* 168 (85% relative intensity, M − 84), which suggests loss of a cyclohexyl radical ($C_6H_{10}D$). Compound **1(3)-d_{16}** has its most intense peaks at *m/e* 340 (100% relative intensity, M$^{\bullet-}$, 256 (20% relative intensity, M − 84), and 168 (45% relative intensity, M − 172). The first fragmentation peak is due to the loss of a $C_6H_{10}D$ radical, while the latter results from loss of a bicyclohexylidene-type radical ($C_{12}H_{10}D_9$) (Scheme 2). For **1(2)-d_4d_4**, the most intense molecular ion peak is found at *m/e* 250 (79% relative intensity, *m/e* 252 expected) while the main fragment peak is located at *m/e* 164 (100% relative intensity, *m/e* 165 expected (M − 87, loss of a $C_6H_7D_4$ radical)). Compound **1(3)-d_4d_4** shows its main molecular ion peak at *m/e* 330 (100% relative intensity, *m/e* 332 expected) and intense fragment peaks at *m/e* 244 (39% relative intensity, *m/e* 245 expected (loss of a $C_6H_7D_4$ radical)) and *m/e* 164 (71% relative intensity, *m/e* 165 expected (loss of a $C_{12}H_{15}D_4$ radical)). The deviations from the expected *m/e* values in the case of **1(2)-d_4d_4** and **1(3)-d_4d_4** can be attributed to the low degree of deuteration of the starting material

Scheme 2. Main Mass Spectral Fragmentation Reactions of Quatercyclohexylidene 1(3)



Scheme 3. Synthetic Scheme for 4″-*tert*-Butyl-1,1′:4′,1″-tercyclohexyliden-4-one 21(2)[a]



[a] (a) BuLi, $(i\text{-Pr})_2NH$, THF; (b) $Me_2NCH(OCH_2CMe_3)_2$, CH_3CN; (c) H_3O^+, THF.

[2,2,6,6-$^2H_4$]cyclohexanone (3% d_1, 18% d_2, 42% d_3, and 37% d_4; see the Experimental Section).

End-Functionalized Oligo(cyclohexylidenes). Despite the fact that the parent compounds **1(*n*)** are obtained in reasonable yield, the observed azine scrambling poses serious problems for the synthesis of higher homologues such as **1(4)** and, especially, for the preparation of end-functionalized derivatives. Moreover, if synthons have to re-enter the reaction cycle to increase oligomer length (*e.g.* **5f** (Scheme 1)), side product formation due to scrambling inevitably will lead to oligomeric mixtures.

Following a different synthetic approach, these problems were solved. The coupling of a ketone to an acid giving a β-hydroxy acid and subsequent decarboxylation and dehydration to yield an alkene is well-documented.[20] If oligo(cyclohexylidene) ketones could re-enter the reaction sequence to obtain longer oligomers, this synthetic strategy could be a useful substitute for the Barton–Kellogg approach. As an example, the synthesis of *tert*-butyl ketone **21(2)** is shown in Scheme 3. Coupling of *tert*-butylcyclohexanecarboxylic acid with monoprotected cyclohexanedione[21] **7** yielded β-hydroxy acid **19** which was decarboxylated and dehydrated[22] to oligo(cyclohexylidene) **20**. After deprotection to ketone **21(1)** followed by reaction with the ethylene acetal of 4-oxocyclohexanecarboxylic acid,[23] ketone **21(2)** was obtained after consecutive decarboxylation, dehydration, and deprotection.

This synthetic strategy is attractive since the use of substituted cyclohexanones and cyclohexanecarboxylic acids gives ready access to monofunctionalized and both symmetrically and asymmetrically α,ω-end-functionalized oligo(cyclohexylidenes). Although the Barton–Kellogg approach can also be applied, oligomeric product mixtures are expected due to scrambling of the asymmetrical azines (*vide supra*). This was confirmed for monoketones **14(1)** and **14(2)** which were synthesized using both strategies. Indeed, using the Barton–Kellogg route, crude monoketone **5f** also contained considerable amounts of diketone **5e** and thiadiazolidine **4a** which were difficult to remove (Scheme 1). Therefore, we strongly favor the decarboxylative–dehydrative pathway for the preparation of asymmetrically substituted oligo(cyclohexylidenes); a variety of end-functionalized oligo(cyclohexylidenes) have been synthesized (Table 3). Introduction of a carbonyl group is readily achieved by using either a monoacetal of cyclohexane-1,4-dione or an acetal of 4-oxocyclohexanecarboxylic acid. Subsequently, the carbonyl group can be converted into a wide range of other functional groups. Furthermore, the carbonyl-containing oligomers can be elongated by reaction with (4-substituted) cyclohexanecarboxylic acid derivatives. Other substituents incorporated include sulfur, alkyl, and alkoxy groups. As anticipated, introduction of alkyl and alkoxy substituents markedly improves the solubility of the oligo(cyclohexylidenes) (*vide supra*). Noteworthy is the fact that a carbonyl group has a similar effect. Some compounds (**11(1)**, **14(1)**, **14(2)**, and **26(1)**) were selectively reduced by catalytic hydrogenation (Pd/C, THF, 1 atm H_2) to the corresponding oligo(cyclohexanes). In short, these synthetic strategies give access to a wide range of mono- and α,ω-end-functionalized oligomers which will be evaluated as molecular building blocks for supramolecular structures.

Table 3. End-Functionalized Oligo(cyclohexylidenes)

compound	*n*	X	Y	synthesis[a]
11(*n*)	1	C=O	C=O	DD
12(*n*)	1	$CHOC_8H_{17}$	$CHOC_8H_{17}$	BK
13(*n*)	1	$CHOC_{10}H_{21}$	$CHOC_{10}H_{21}$	BK
14(*n*)	1, 2, 3	CH_2	C=O	DD/BK
18(*n*)	1	CH_2	$CHOC_8H_{17}$	DD
21(*n*)	1, 2	CH-*t*-Bu	C=O	DD
26(*n*)	1	CHC_7H_{15}	C=O	DD
28(*n*)	2	CH_2	CHC_7H_{15}	DD
30(*n*)	2	CHC_7H_{15}	CHC_7H_{15}	DD
32(*n*)	1, 2	CH_2	S	DD
35(*n*)	1, 2	C=O	S	DD
41(*n*)	1	CH_2	CHOH	DD

[a] BK: Barton–Kellogg olefin synthesis. DD: decarboxylative dehydration of β-hydroxy acids.

Molecular Structure and Rod Length. Molecular mechanics (MMX),[24a] semiempirical (AM1),[24b] and *ab initio* calculations (6-31G basis set)[10] predict that oligo-

(17) Bicyclohexylidene exhibits approximate C_{2h} symmetry in the solid state;[18] *ab initio* calculations at the HF/6-31G level show a genuine minimum for **1(*n*)** (*n* = 1–3) in C_{2h} symmetry.[10]

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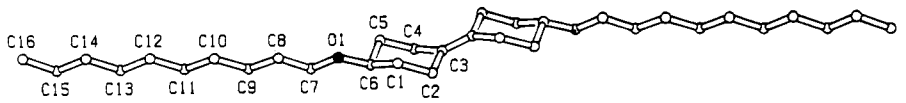

Figure 1. PLUTON representation of the single-crystal X-ray structure of *trans*-4,4′-bis(decyloxy)-1,1′-bicyclohexylidene **13(1)** with the adopted atom-numbering scheme. Hydrogen atoms are omitted for clarity.

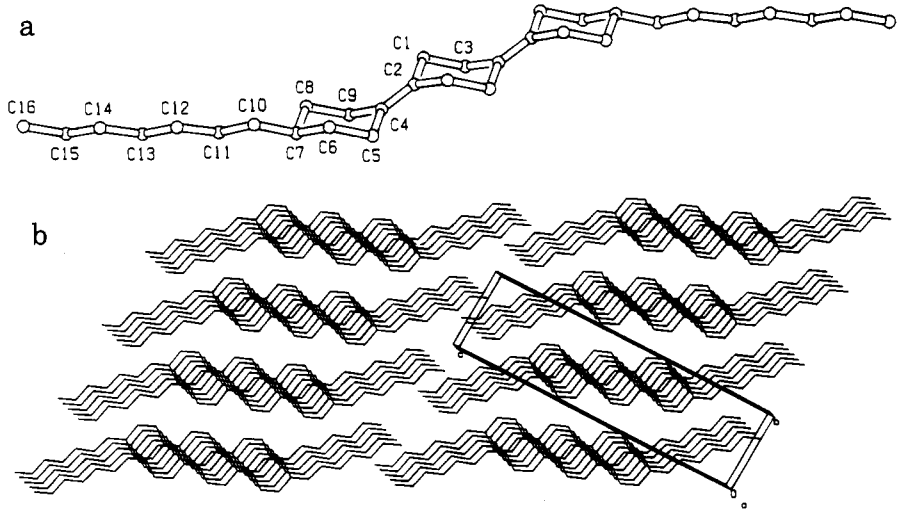

Figure 2. (a) PLUTON representation of the single-crystal X-ray structure of *trans*-4,4″-diheptyl-1,1′:4′,1″-tercyclohexylidene **30(2)** with the adopted atom-numbering scheme. Hydrogen atoms are omitted for clarity. (b) Perspective view of the molecular packing of **30(2)**.

Table 4. Lengths of Oligo(cyclohexylidenes) 1(*n*) Calculated by Semiempirical and *ab Initio* Methods

n	H··H length[a]	C··C length[b]
1	9.05 (9.03)[c]	7.11 (7.16)
2	13.15 (13.19)	11.29 (11.39)
3	17.33 (17.35)	15.48 (15.60)
4	21.43	19.64

[a] Distance (Å) between the two equatorial terminal hydrogen atoms calculated using the AM1 Hamiltonian.[22] [b] Distance (Å) between two terminal carbon atoms calculated using the AM1 Hamiltonian. [c] Single-crystal X-ray structure: 8.88 Å.[18] Values in parentheses calculated by *ab initio* methods using the 6-31G basis set.[10]

(cyclohexylidenes) **1(*n*)** possess extended, chairlike geometries in their equilibrium structure; concomitant with increasing ***n***, an average increment of 4.1 Å is found (Table 4). In line with the calculated data, a rodlike structure is found in the single-crystal X-ray structure of bicyclohexylidene **1(1)**.[18] Interestingly, a similar structure is observed for alkoxy-substituted derivatives **12(1)** and **13(1)**. Figure 1 shows a PLUTON[25] drawing of the single-crystal X-ray structure of *trans*-4,4′-bis(decyloxy)-1,1′-bicyclohexylidene **13(1)**. The cyclohexyl-type rings adopt a chairlike geometry, and the molecule possesses a center of inversion located at the center of the C–C double bond (C_i symmetry). The geometry of the bicyclohexylidene part is comparable to that of **1(1)**. The alkoxy groups show a deviation from the long axis of the bicyclohexylidene skeleton (C6–C6′) of 21° (180° – the C16–C6–C6′ angle = 21.57(4)°). The alkoxy chains do not intercalate, leading to a packing motif of layers of molecules parallel to the *ab* plane.[26] Unfortunately, we were unable to obtain suitable crystals for X-ray analysis of compounds **1(*n*)** with ***n*** > 1. Nevertheless, wide angle X-ray powder diffraction (WAXD) gave for all compounds **1(*n*)** (***n*** = 1–3) a strong reflection at a *d* value of 4.1 Å. Comparison with the calculated WAXD pattern from the X-ray structure of **1(1)** indicates that the 4.1 Å spacing (*d* 1 0 −1) is typical for the close-contact distance between the cyclohexyl-type rings of the rods. This strongly suggests that compounds **1(*n*)** possess similar packing motifs independent of their length. This is further supported by the decreasing solubility and increasing thermal stability concomitant with increasing ***n*** (*vide supra*). X-ray quality single crystals were obtained for *trans*-4,4″-diheptyl-1,1′:4′,1″-tercyclohexylidene **30(2)**. Figure 2a shows a PLUTON representation of the molecular structure. As anticipated from the WAXD data of compounds **1(*n*)** and the results of our calculations, the three cyclohexyl-type rings adopt a chairlike structure. The molecule possesses a center of inversion located in the center of the middle ring (C_i symmetry). A C_{term}–C_{term} (C7–C7′) distance of 11.42 Å is found for the tercyclohexylidene skeleton which is in excellent agreement with the calculated (6-31G basis set) value of 11.39 Å for **1(2)** (Table 4). The alkyl chains adopt an antiperiplanar conformation; they deviate from the long molecular axis (C7–C7′) of the tercyclohexylidene skeleton by 27° (180° – the C16–C7–C7′ angle = 27.02(4)°). Again, layers parallel to the *ab* plane are found in the solid state; the alkyl groups do not intercalate (Figure 2b).

A comparison of the packing coefficients of **12(1)** (68.9%), **13(1)** (65.2%), and **30(2)** (68.1%) with that of bicyclohexylidene **1(1)** (71.2%) reveals the relatively dense packing of the oligo(cyclohexylidene) frameworks. From the X-ray structural data, it is concluded that the oligo(cyclohexylidene) frameworks stack in a highly ordered fashion which may be valuable with respect to their use as molecular building blocks.

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(26) A similar geometry and packing motif is found for *trans*-4,4′-bis(octyloxy)-1,1′-bicyclohexylidene **12(1)** (see the Experimental Section).

Conclusion

Oligo(cyclohexylidenes) form a new class of molecular rodlike materials which can be obtained *via* either of the two described synthetic pathways. From their low solubility, high melting point, and powder diffraction pattern, a highly ordered structure in the solid state is anticipated. This is confirmed by single-crystal X-ray analyses. End-functionalized derivatives are readily accessible, allowing for the study of self-assembly and charge-transfer phenomena. Experiments are in progress, and results will be published in due course.

Experimental Section

All reactions were carried out under a dry N_2 atmosphere unless stated otherwise. Commercially available reagents were used without purification. Solvents were dried using standard procedures. NMR spectra were recorded at 300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR, 46 MHz for ^{2}H NMR, and 121 MHz for ^{31}P NMR. Chemical shifts are given relative to external TMS (^{1}H, ^{2}H, and ^{13}C) or 85% phosphoric acid (^{31}P). Samples were dissolved in deuterated chloroform (^{1}H, ^{13}C, and ^{31}P) or chloroform containing 0.1 mL of deuterated chloroform (^{2}H). Differential scanning calorimetry (DSC, Mettler DSC 12E apparatus) was done using a heating and cooling rate of 5 °C/min. Thermogravimetry (TGA, Perkin-Elmer TGS-2 Thermogravimetric System) was performed under either air or a N_2 atmosphere: heating rate 20 °C/min. Elemental analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. WAXD patterns were obtained at ambient temperature using a Delft Instruments Guinier Johansson FR552 camera at a wavelength of 1.5405 Å.

Single-Crystal X-ray Structure of 12(1), 13(1), and 30(2).[27] Crystal data for compound **12(1)** were as follows: $C_{28}H_{52}O_2$, M_r = 420.72, colorless plate-shaped crystal (0.55 × 0.3 × 0.01 mm), space group $P\bar{1}$ with a = 5.225(15) Å, b = 6.289(4) Å, c = 19.99(8) Å, α = 91.23(17)°, β = 94.5(3)°, γ = 103.94(13)°, V = 635(3) Å^3, Z = 1, D_c = 1.100 g cm^{-3}, $F(000)$ = 236, μ(Mo Kα) = 0.6 cm^{-1}, 1853 reflections measured, 1669 independent reflections (1.02° < θ < 22.49°, T = 150 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å) on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Data were corrected for Lp (Lorentz-polarization) effects and for instability; empirical absorption correction was applied (DIFABS[28]). The structure was solved by automated direct methods (SHELXS86[29]). Refinement of F^2 was carried out by full-matrix least-squares techniques (SHELXL-93[30]). Refinement converged at a final $R2_w$ value of 0.364, $R1$ = 0.133 (for 438 reflections with $F_o > 4\sigma(F_o)$), S = 0.90 for 136 parameters. No residual density was found outside −0.37 and 0.38 e Å^{-3}. The relatively high R values are due to the poor diffraction properties of the best available crystals.

Crystal data for compound **13(1)** were as follows: $C_{32}H_{60}O_2$, M_r = 476.83, colorless plate-shaped crystal (0.8 × 0.8 × 0.05 mm), space group $P\bar{1}$ with a = 5.4064(9) Å, b = 6.3591(13) Å, c = 23.116(9) Å, α = 94.88(2)°, β = 91.56(2)°, γ = 103.632(15)°, V = 768.6(4) Å^3, Z = 1, D_c = 1.030 g cm^{-3}, $F(000)$ = 268, μ(Cu Kα) = 4.3 cm^{-1}, 3750 reflections measured, 3156 independent reflections (1.92° < θ < 74.96°, T = 295 K, Cu Kα radiation, Ni filter, λ = 1.541 84 Å) on an Enraf-Nonius CAD4-F diffractometer. Data were corrected for Lp effects and for linear decay of 4%; empirical absorption correction was applied (DIFABS[28]). The structure was solved by automated direct methods (SIR92[31]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93[30]). Refinement converged at a final $R2_w$ value of 0.187, $R1$ = 0.064 (for 1278 reflections with $F_o > 4\sigma(F_o)$), S = 0.85 for 155 parameters. No residual density was found outside −0.16 and 0.25 e Å^{-3}.

Crystal data for compound **30(2)** were as follows: $C_{32}H_{56}$, M_r = 440.80, colorless block-shaped crystal (0.40 × 0.25 × 0.15 mm), space group $P\bar{1}$ with a = 4.4917(4) Å, b = 6.7765(6) Å, c = 23.8534(14) Å, α = 95.152(6)°, β = 90.102(6)°, γ = 105.925(7)°, V = 695.1(1) Å^3, Z = 1, D_c = 1.053 g cm^{-3}, $F(000)$ = 248, μ(Mo Kα) = 0.6 cm^{-1}, 6206 reflections measured, 3179 independent reflections (0.90° < θ < 27.50°, T = 150 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å) on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Data were corrected for Lp effects and for linear decay of 14% but not for absorption. The structure was solved by automated direct methods (SHELXS86[29]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93[30]). Refinement converged at a final $R2_w$ value of 0.219, $R1$ = 0.078 (for 1589 reflections with $F_o > 4\sigma(F_o)$), S = 1.01 for 146 parameters. No residual density was found outside −0.28 and 0.29 e Å^{-3}.

1,4-Cyclohexanedione Bis(diethoxyphosphinyl)hydrazone (9). To a stirred mixture of diethyl phosphorohydrazidate[32] (8.45 g, 50.3 mmol), sodium sulfate (30 g), and acetic acid (0.1 mL) in dichloromethane (150 mL) was added a solution of 2.80 g (25.0 mmol) of cyclohexane-1,4-dione in dichloromethane (100 mL). After stirring overnight at room temperature, the reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The crude product was recrystallized from acetone, yielding 7.71 g of a green solid (18.7 mmol, 75%) as a mixture of syn/anti isomers: mp 175 °C dec; ^{1}H NMR δ 7.65, 7.43 (d, J_{PH} = 26 Hz, 2 H), 4.06 (m, 8 H), 2.58 (m, 4 H), 2.39 (m, 4 H), 1.27 (t, 12 H); ^{13}C NMR δ 153.66, 153.43, 63.07, 63.00, 31.61, 29.40, 24.80, 22.25, 16.13, 16.03; ^{31}P NMR δ 4.06; IR (KBr) 3180, 2978, 2931, 2905, 2870, 1637, 1437 cm^{-1}.

Parent Oligo(cyclohexylidenes): Barton–Kellogg Route. 1,1′-Bicyclohexylidene (1(1)). A solution of thiadiazoline **4a** (29.5 g, 0.131 mol) in toluene (1000 mL) was refluxed for 2 h. After the solution was cooled to room temperature, triethyl phosphite (114.5 g, 0.69 mol) was added, and the reaction mixture was refluxed overnight. The yellow solution was cooled to room temperature, and the solvent was removed *in vacuo*. The pale yellow solid was recrystallized from methanol (250 mL), yielding 17.21 g (105 mmol, 80%) of white needles: mp 55.6 °C (lit.[13a] 53–55.5 °C); ^{1}H NMR δ 2.17 (m, 8 H), 1.42–1.61 (m, 12 H); ^{13}C NMR δ 129.42, 30.11, 28.71, 27.29; IR (KBr) 2921, 2912, 2854, 2840, 1442, 1432, 1012, 609 cm^{-1}; GC/MS *m/e* 164 (M$^{+\cdot}$). Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.64; H, 12.37.

1,1′:4′,1″-Tercyclohexylidene (1(2)). A suspension of bisthiadiazoline **4b** (7.00 g, 19.2 mmol) was refluxed in toluene (250 mL) for 2.5 h. After the solution was cooled to room temperature, triethyl phosphite (15.94 g, 96.0 mmol) was added, and the reaction mixture was refluxed overnight. Upon the solution being cooled to room temperature, a solid precipitated and was filtered off. The filtrate was subjected to flash chromatography (silica; eluent, toluene), concentrated *in vacuo*, and recrystallized from cyclohexane, yielding 0.84 g of a white solid. Recrystallization of the initially formed precipitate from cyclohexane afforded a small amount of a solid which was discarded since it consisted mainly of **1(3)** as evidenced by ^{1}H NMR. The filtrate was subjected to flash chromatography (silica; eluent, toluene), and after solvent removal and recrystallization from cyclohexane, another 1.07 g of a white solid was obtained: total yield 1.91 g (7.81 mmol, 41%); mp 159–164 °C; ^{1}H NMR δ 2.26 (s, 8 H), 2.18 (m, 8 H), 1.44–1.62 (m, 12 H); ^{13}C NMR δ 130.15, 128.03, 30.13, 29.38, 28.46, 27.19; IR (KBr) 2978, 2921, 2851, 2671, 1447, 1431, 1009 cm^{-1}; GC/MS *m/e* 244 (M$^{+\cdot}$). Anal. Calcd for $C_{18}H_{24}$: C, 88.45; H, 11.55. Found: C, 88.26; H, 11.60.

(27) Atomic coordinates (including calculated H atom coordinates), thermal parameters, bond lengths, and bond angles for the crystal structure determination of compounds **12(1)**, **13(1)**, and **30(2)** have been deposited at the Cambridge Crystallographic Data Centre. They can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 IEZ, U.K.

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1,1′:4′,1″:4″,1‴-Quatercyclohexylidene (1(3)). A suspension of terthiadiazoline **4c** (2.37 g, 4.70 mmol) in toluene (250 mL) was heated to reflux for 5 h. After the mixture was cooled to room temperature, triethyl phosphite (11.7 g, 70.5 mmol) was added, and the reaction mixture was refluxed overnight. Upon the mixture being cooled to room temperature, a white precipitate which was isolated by filtration formed, yielding 1.20 g (3.70 mmol, 79%) of a white powder: mp 200 °C dec; ^{1}H NMR δ 2.27 (s, 16 H), 2.18 (m, 8 H), 1.54 (m, 12 H); ^{13}C NMR (318 K) δ 130.20, 128.80, 128.64, 30.14, 29.43, 29.14, 28.46, 27.19; IR (KBr) 2976, 2922, 2852, 2673, 1446, 1431, 1010, 658 cm^{-1}; GC/MS *m/e* 324 (M$^{\bullet+}$). Anal. Calcd for $C_{24}H_{36}$: C, 88.82; H, 11.18. Found: C, 88.68; H, 10.96.

1,1′:4′,1″:4″,1‴:4‴,1⁗-Quinquecyclohexylidene (1(4)). A suspension of quaterthiadiazoline **4d** (1.20 g, 1.86 mmol) in toluene (700 mL) was refluxed for 2 h. After the mixture was cooled to room temperature, triethyl phosphite (13.2 g, 79.5 mmol) was added, and the reaction mixture was refluxed overnight. The hot reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The crude solid product was sublimed (0.05 mmHg, 130 °C). The residue of the sublimation was a white powder (0.50 g, 1.24 mmol, 67%) which decomposes at 270 °C: IR (KBr) 2977, 2959, 2922, 2897, 2882, 2839, 1460, 1443, 1431 cm^{-1}; direct inlet GC/MS *m/e* 404 (M$^{\bullet+}$), purity approximately 80%; impurities *m/e* 324 (M$^{\bullet+}$, quatercyclohexylidene **1(3)**), 484 (M$^{\bullet+}$, sexicyclohexylidene **1(5)**).

Deuterated Tercyclohexylidenes 1(2)-d_4d_4 and 1(2)-d_8: Barton–Kellogg Route. Compounds **1(2)-d_4d_4** and **1(2)-d_8** were synthesized starting from [2,2,6,6-$^2H_4$]cyclohexanone and [$^2H_8$]cyclohexane-1,4-dione using the approach as outlined above for tercyclohexylidene **1(2)**.

[2,2,6,6-$^2H_4$]Cyclohexanone. Cyclohexanone (20.0 g, 0.20 mol) was stirred with P_2O_5 (0.7 g) in D_2O (20 mL) for 4 days at 50 °C.[33] The layers were separated, and the cyclohexanone was washed with a small quantity of water and dried over $MgSO_4$. The complete produce was repeated four times, after which the deuterated cyclohexanone was purified using vacuum distillation (48 °C, 15 mmHg): ^{1}H NMR δ 1.40 (m, 4 H), 1.25 (m, 2 H); ^{13}C NMR δ 210.35, 40.97, 26.50, 24.50; isotopic purity 3% d_1, 18% d_2, 42% d_3, 37% d_4 (GC/MS).

[2,2,6,6-$^2H_4$]Cyclohexanone Diethoxyphosphinylhydrazone (6-d_4). Compound **6-d_4** was synthesized according to a literature procedure[15] using equimolar amounts of [2,2,6,6-$^2H_4$]cyclohexanone and diethyl phosphorohydrazidate:[32] yield 7.31 g (29.0 mmol, 97%). The crude white solid was used in the next reaction step without recrystallization: ^{1}H NMR δ 7.10 (d, J_{PH} = 26 Hz, 1 H), 4.05 (m, 4 H), 1.55 (s, 6 H), 1.25 (t, J = 8.7 Hz, 6 H); ^{13}C NMR δ 156.31, 156.06, 62.92, 62.85, 26.89, 26.81, 25.65, 25.58, 16.11, 16.02.

[2,2,6,6,2″,2″,6″,6″-$^2H_8$]-1,1′:4′,1″-Tercyclohexylidene (1(2)-d_4d_4). A suspension of bisthiadiazoline **4b-d_4d_4** (0.62 g, 1.67 mmol) was refluxed in toluene (350 mL) for 2 h. After the mixture was cooled to room temperature, triethyl phosphite (2.80 g, 16.9 mmol) was added, and the mixture was refluxed overnight. After removal of the solvents *in vacuo* and recrystallization from *tert*-butyl methyl ether, a white solid was obtained. The yield of the crude material was 0.26 g (1.03 mmol, 65%). About 50 mg of the crude white solid was purified by sublimation (0.2 mmHg, 100 °C): ^{1}H NMR δ 2.25 (s, 8 H), 1.50 (m, 12 H); ^{13}C NMR δ 130.06, 128.03, 29.41, 28.40, 27.13; ^{2}H NMR δ 2.16 (s); IR (KBr) 2969, 2921, 2882, 2851, 2839, 2217 (CD), 2132 (CD), 2103 (CD), 2091 (CD), 2076 (CD), 1442 cm^{-1}; isotopic purity 1% d_2, 5% d_3, 14% d_4, 24% d_5, 28% d_6, 20% d_7, 7% d_8; isotopic composition of the scrambling product **1(3)-d_4d_4** 2% d_2, 5% d_3, 14% d_4, 22% d_5, 28% d_6, 20% d_7, 8% d_8 (GC/MS).

[$^2H_8$]Cyclohexane-1,4-dione. A mixture of cyclohexane-1,4-dione (10.10 g, 90.2 mmol) and P_2O_5 (0.5 g) in D_2O (20 mL) was stirred for 3 days at 50 °C.[33] The reaction mixture was then extracted five times using 30 mL quantities of dichloromethane. The combined extracts were dried over $MgSO_4$, and the solvent was removed *in vacuo*. The complete procedure was repeated three times: yield 6.71 g (55.9 mmol, 62%); ^{13}C NMR δ 213.25, 40.55 (q); IR (KBr) 2220, 2120, 1720 cm^{-1}; isotopic purity 1% d_5, 3% d_6, 14% d_7, 82% d_8 (GC/MS).

[2′,2′,3′,3′,5′,5′,6′,6′-$^2H_8$]-1,1′:4′,1″-Tercyclohexylidene (1(2)-d_8). A suspension of bisthiadiazoline **4b-d_8** (1.50 g, 4.03 mmol) was refluxed in toluene (500 mL) for 2 h. After the mixture was cooled to room temperature, triethyl phosphite (7.00 g, 42.2 mmol) was added, and the reaction mixture was refluxed overnight. After removal of the solvents *in vacuo*, a white solid was obtained. The crude white solid was purified by recrystallization, first from cyclohexane and then from *n*-hexane. The resulting material was subjected to column chromatography (silica; eluent, cyclohexane) to give the tercyclohexylidene: 151 mg (0.60 mmol, 15%); ^{1}H NMR δ 2.15 (m, 8 H), 1.55 (m, 12 H); ^{13}C NMR δ 130.15, 128.00, 30.14, 28.50, 27.22; ^{2}H NMR δ 2.23 (s); IR (KBr) 2973, 2921, 2891, 2852, 2838, 2100 (CD), 2083 (CD), 1459, 1445 cm^{-1}; isotopic purity 1% d_4, 2% d_5, 6% d_6, 27% d_7, 55% d_8; isotopic composition of the scrambling product **1(3)-d_{16}** 1% d_{11}, 2% d_{12}, 4% d_{13}, 12% d_{14}, 31% d_{15}, 45% d_{16} (GC/MS).

End-Functionalized Oligo(cyclohexylidenes): Barton–Kellogg Route. 1,1′-Bicyclohexylidene-4,4′-dione (11(1)). Dione **11(1)** was synthesized by refluxing bisacetal **10(1)** (2.69 g, 7.38 mmol) in a mixture of THF (25 mL) and 2 M hydrochloric acid (25 mL) for 1 h. THF was removed *in vacuo*, and the resulting suspension was extracted with dichloromethane (5 × 20 mL). After the combined organic fractions were washed with saturated $NaHCO_3$ solution and water and dried ($MgSO_4$) and the solvent was removed, the diketone was obtained quantitatively. A small amount was recrystallized from *n*-hexane: mp 116–117 °C (lit.[12f,g] 121–122 °C, 117–118 °C); ^{1}H NMR δ 2.54 (m, 8 H), 2.38 (m, 8 H); ^{13}C NMR δ 212.02, 127.48, 39.85, 26.48; IR (KBr) 2970, 2905, 2858, 1710, 1448, 1420 cm^{-1}.

4,4′-Bis(octyloxy)-1,1′-bicyclohexylidene (12(1)). Crude thiadiazoline **4h** (4.70 g, 9.78 mmol) was refluxed in toluene (300 mL) for 3 h. After the mixture was cooled to room temperature, triethyl phosphite (17.0 g, 0.10 mol) was added, and the mixture was refluxed overnight. Removal of solvent under reduced pressure afforded a yellow oil which on trituration with a 1:1 mixture of ethanol and methanol solidified, yielding 3.40 g (8.08 mmol, 83%) of a white solid. The solid consisted of the *trans* and *cis* isomers in a ratio of *ca.* 3:2 (GC). Repeated recrystallization (three times) from ethanol/methanol (1:1 v/v) afforded 0.90 g (2.14 mmol) of the pure 4,4′-*trans* isomer: mp 48.0 °C; ^{1}H NMR δ 3.42 (m, 6 H), 2.55 (m, 4 H), 1.87 (m, 8 H), 1.55 (m, 4 H), 1.30 (m, 24 H), 0.84 (t, 6 H); ^{13}C NMR δ 128.60, 76.63, 68.07, 33.18, 31.85, 30.25, 29.49, 29.31, 26.48, 26.28, 22.67, 14.11; IR (KBr) 2930, 2926, 2920, 2851, 1466, 1365, 1096 cm^{-1}; GC/MS *m/e* 420 (M$^{\bullet+}$). Anal. Calcd for $C_{28}H_{52}O_2$: C, 79.94; H, 12.46; O, 7.61. Found: C, 80.02; H, 12.38; O, 7.48.

4,4′-Bis(decyloxy)-1,1′-bicyclohexylidene 13(1). Crude thiadiazoline **4i** (1.73 g, 3.22 mmol) was refluxed in toluene (100 mL) for 3 h. After the mixture was cooled to room temperature, triethyl phosphite (5.30 g, 32.0 mmol) was added, and the mixture was refluxed overnight. Removal of the solvent under reduced pressure afforded a yellow oil which on trituration with a 1:1 mixture of ethanol and methanol solidified, yielding 1.30 g (2.73 mmol, 85%) of a white solid. The solid consisted of the *trans* and *cis* isomers in a ratio of *ca.* 3:2 (GC). Repeated recrystallization (three times) from ethanol/methanol (1:1 v/v) gave 0.51 g (1.07 mmol) of the pure 4,4′-*trans* isomer: mp 58.6 °C; ^{1}H NMR δ 3.42 (m, 6 H), 2.55 (m, 4 H), 1.87 (m, 8 H), 1.55 (m, 4 H), 1.30 (m, 32 H), 0.86 (t, 6 H); ^{13}C NMR δ 128.63, 76.79, 68.10, 33.19, 31.90, 30.25, 29.62, 29.57, 29.51, 29.31, 26.48, 26.26, 22.67, 14.09; IR (KBr) 2930, 2921, 2849, 1467, 1102, 1094 cm^{-1}; GC/MS *m/e* 476 (M$^{\bullet+}$). Anal. Calcd for $C_{32}H_{60}O_2$: C, 80.61; H, 12.68. Found: C, 79.46; H, 12.44.

1,1′-Bicyclohexyliden-4-one (14(1)). Ketone **5f** (3.34 g, 14.0 mmol) was refluxed in toluene (150 mL) for 3 h. After the mixture was cooled to room temperature, triethyl phosphite (11.65 g, 70.1 mmol) was added, and the mixture was refluxed overnight. After evaporation of the solvent *in vacuo*, a colorless oil was obtained which was dissolved in *n*-hexane

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(100 mL) and stirred overnight with a saturated $NaHSO_3$ solution (200 mL). The resulting white solid was filtered off, washed with *n*-hexane, and suspended in dichloromethane. After the mixture was stirred with a saturated Na_2CO_3 solution until all the solid material dissolved, the layers were separated and the organic layer was dried ($MgSO_4$). The solvent was removed under reduced pressure, and 1.10 g (6.18 mmol, 44%) of a white solid was obtained: mp 52.5 °C; ^1H NMR δ 2.43 (m, 4 H), 2.30 (m, 4 H), 2.10 (m, 4 H), 1.45 (m, 6 H); ^{13}C NMR δ 212.87, 133.70, 123.17, 40.87, 30.34, 28.23, 26.86, 26.54; IR (KBr) 2960, 2925, 2920, 1715, 1450, 1420 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18; O, 8.97. Found: C, 80.65; H, 10.26; O, 9.02.

1,1′:4′,1″-Tercyclohexyliden-4-one (14(2)). Ketone **5j** (10.0 g, 26.4 mmol) was refluxed in toluene (1000 mL) for 3 h. Triethyl phospite (46.0 g, 0.28 mol) was added, and the mixture was refluxed overnight. After solvent removal under reduced pressure, a sticky yellow solid was obtained, which was suspended in boiling *tert*-butyl methyl ether (800 mL). An insoluble solid was filtered off (hot), and this solid was again suspended in boiling *tert*-butyl methyl ether. Again, not all the material dissolved, and hot filtration afforded 2.40 g (9.30 mmol, 35%) of **5j** as a white solid in a purity of approximately 94% (^1H NMR). The filtrate of the first hot filtration was evaporated to dryness and recrystallized from *n*-hexane (400 mL) in order to remove bicyclohexylidene-type side products. The resulting white solid was subjected to flash chromatography (silica; eluent, chloroform/acetone (10:1 v/v)) to remove phosphorus compounds. Solvent removal *in vacuo* and recrystallization of the obtained solid from *tert*-butyl methyl ether (50 mL) afforded 0.50 g (1.94 mmol, 7.3%) of a white solid with correct analytical data: mp 152 °C dec; ^1H NMR δ 2.57 (m, 4 H), 2.45 (m, 4 H), 2.25 (s, 8 H), 2.18 (m, 4 H), 1.55 (m, 6 H); ^{13}C NMR δ 212.85, 132.36, 130.78, 126.92, 123.90, 40.52, 30.08, 29.49, 28.67, 28.33, 27.05, 26.46; IR (KBr) 2976, 2958, 2926, 1721, 1447, 1419 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 82.80; H, 10.08.

End-Functionalized Oligo(cyclohexylidenes): Decarboxylative Dehydration of β-Hydroxy Acids. 1,1′-Bicyclohexyliden-4-one (14(1)). Acetal **16(1)** (13.43 g, 51.4 mmol) was dissolved in THF (150 mL), and 2 M hydrochloric acid (150 mL) was added. The mixture was heated to reflux for 1 h. After the mixture was cooled to room temperature, THF was removed *in vacuo*, and the resulting white suspension was extracted with 5 portions of 50 mL of dichloromethane. After the combined organic extracts were washed with saturated $NaHCO_3$ solution and water and dried ($MgSO_4$) and the solvent was evaporated, a white solid was obtained in quantitative yield: mp 50 °C. The analytical data were identical to those of the ketone obtained *via* the Barton–Kellogg synthesis.

1,1′:4′,1″-Tercyclohexyliden-4-one (14(2)). Hydrolysis of acetal **16(2)** (2.47 g, 7.18 mmol) as described for **14(1)** afforded quantitatively ketone **14(2)**, mp 147 °C, with analytical data identical to those of the ketone obtained *via* the Barton–Kellogg synthesis.

1,1′:4′,1″:4″,1‴-Quatercyclohexyliden-4-one (14(3)). Due to the insolubility of acetal **16(3)** (182 mg, 0.43 mmol) in THF, the deprotection reaction was carried out in a mixture of 1,2-dichloroethane (100 mL) and 5% hydrochloric acid (100 mL). After the mixture was refluxed for 12 h, 1,2-dichloroethane was removed *in vacuo*, and the water layer was extracted with chloroform (3 × 100 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (150 mL) and water (50 mL). After drying ($MgSO_4$) and solvent removal under reduced pressure, ketone **14(3)** was isolated in quantitative yield: mp 190 °C dec; ^1H NMR δ 2.57 (m, 4 H), 2.41 (m, 4 H), 2.28 (s, 8 H), 2.25 (s, 8 H), 2.17 (m, 4 H), 1.53 (m, 6 H); ^{13}C NMR δ 213.01, 132.39, 130.42, 129.59, 127.81, 127.71, 123.98, 40.58, 30.14, 29.43, 29.31, 29.03, 28.76, 28.44, 27.16, 26.53; IR (KBr) 2974, 2959, 2924, 2884, 2839, 1723, 1445, 1431 cm^{-1}.

4-(Octyloxy)-1,1′-bicyclohexylidene (18(1)). β-Hydroxy acid **17** (1.68 g, 4.74 mmol) and *N,N*-dimethylformamide dineopentyl acetal (2.20 g, 9.49 mmol) in acetonitrile (50 mL) were stirred for 1 h at room temperature, after which the reaction mixture was heated to reflux overnight. Solvent removal under reduced pressure afforded a yellow oil which was subjected to flash chromatography (silica; eluent, *n*-hexane). A white solid was isolated (0.20 g, 0.68 mmol, 15%): mp 23.5 °C; ^1H NMR δ 3.44 (m, 3 H), 2.54 (m, 2 H), 2.19 (m, 4 H), 1.89 (m, 4 H), 1.60–1.20 (m, 20 H), 0.89 (t, 3 H); ^{13}C NMR δ 130.23, 127.53, 76.99, 67.96, 33.25, 31.76, 30.18, 29.40, 29.21, 28.53, 27.09, 26.29, 26.21, 22.57, 13.96; IR (NaCl) 2940, 2860, 1449, 1105 cm^{-1}.

4′-*tert*-Butyl-1,1′-bicyclohexyliden-4-one (21(1)). Hydrolysis of **20** (9.50 g, 29.7 mmol) as described for **14(1)** afforded quantitatively ketone **21(1)**: mp 68 °C; ^1H NMR δ 2.65 (m, 2 H), 2.48 (m, 4 H), 2.30 (m, 4 H), 1.80 (m, 2 H), 1.55 (m, 2 H), 1.13 (m, 1 H), 0.90 (m, 2 H), 0.75 (s, 9 H); ^{13}C NMR δ 212.38, 133.28, 122.89, 48.29, 40.74, 32.33, 29.97, 28.69, 27.54, 26.54; IR (KBr) 2980, 2958, 2937, 2912, 2895, 2858, 2833, 1713, 1469, 1456, 1438, 1417 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18; O, 6.83. Found: C, 81.74; H, 11.13; O, 7.06.

4″-*tert*-Butyl-1,1′:4′,1″-tercyclohexyliden-4-one (21(2)). Acetal **23** (513 mg, 1.43 mmol) was hydrolyzed by refluxing it in a mixture of THF (25 mL) and 2 M hydrochloric acid (20 mL) for about 10 min. After evaporation of THF, the resulting suspension was extracted with dichloromethane (3 × 30 mL). After the organic fractions were washed with saturated $NaHCO_3$ solution and dried ($MgSO_4$) and the solvent was evaporated, 431 mg of a white solid (1.37 mmol, 96%) was obtained. Since the crude product contained some starting compound, it was subjected to column chromatography (silica; eluent, dichloromethane). The first fractions contained pure ketone **14** (150 mg): mp 135 °C; ^1H NMR δ 2.74 (m, 2 H), 2.57 (m, 4 H), 2.41 (m, 4 H), 2.28 (s, 8 H), 1.85 (m, 2 H), 1.67 (m, 2 H), 1.15 (m, 1 H), 0.92 (m, 2 H), 0.80 (s, 9 H); ^{13}C NMR δ 212.97, 132.45, 130.65, 126.72, 123.98, 48.46, 40.59, 32.43, 29.84, 29.53, 28.89, 28.77, 27.62, 26.54; IR (KBr) 2965, 2938, 2910, 2864, 2837, 1721, 1476, 1466, 1445 cm^{-1}.

4′-Heptyl-1,1′-bicyclohexyliden-4-one (26(1)). Hydrolysis of acetal **25** (3.21 g, 8.80 mmol) as described for **14(1)** afforded ketone **26(1)** in quantitative yield: mp 47 °C; ^1H NMR δ 2.66 (m, 2 H), 2.50 (m, 4 H), 2.40 (m, 4 H), 1.81 (m, 4 H), 1.36–1.14 (m, 14 H), 0.96 (m, 1 H), 0.89 (t, 3 H); ^{13}C NMR δ 212.92, 133.62, 123.11, 40.83, 37.74, 36.71, 34.42, 31.88, 29.91, 29.56, 29.32, 27.04, 26.61, 22.65, 14.06; IR (KBr) 2955, 2922, 2870, 1711, 1464, 1443, 1109 cm^{-1}. Anal. Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found: C, 82.33; H, 11.51.

4-Heptyl-1,1′:4′,1″-tercyclohexylidene (28(2)). β-Hydroxy acid **27** (1.25 g, 3.10 mmol) and *N,N*-dimethylformamide dineopentyl acetyl (1.64 g, 7.10 mmol) in acetonitrile (50 mL) were stirred at room temperature for 1 h. The reaction mixture was heated to reflux overnight, and after the mixture was cooled to −10 °C, solid **28(2)** was filtered off (0.79 g, 2.30 mmol, 75%): mp 113–114 °C; ^1H NMR δ 2.67 (m, 2 H), 2.32–2.13 (m, 14 H), 1.83–1.56 (m, 4 H), 1.49 (m, 6 H), 1.42–1.10 (m, 12 H), 0.96–0.81 (m, 4 H); ^{13}C NMR δ 130.14, 130.09, 128.02, 38.02, 36.91, 34.70, 31.92, 30.13, 29.97, 29.48, 29.38, 29.34, 28.47, 27.20, 27.10, 22.70, 14.12; IR (KBr) 2982, 2957, 2917, 2849, 2837, 1464, 1449, 1427 cm^{-1}. Anal. Calcd for $C_{25}H_{42}$: C, 87.64; H, 12.36. Found: C, 87.54; H, 12.31.

4,4″-Diheptyl-1,1′:4′,1″-tercyclohexylidene (30(2)). Reaction of β-hydroxy acid **29** (1.65 g, 4.49 mmol) and *N,N*-dimethylformamide dineopentyl acetal (2.08 g, 9.00 mmol) in acetonitrile (50 mL) as described for **28(2)** yielded 1.22 g (2.78 mmol, 62%) of the alkene as a mixture of *cis* and *trans* isomers in a ratio of *ca.* 1:1 (GC). Recrystallization from chloroform afforded the pure *trans* isomer: mp 131 °C; ^1H NMR δ 2.64 (m, 4 H), 2.23 (m, 8 H), 1.72 (m, 8 H), 1.35–1.11 (m, 28 H), 0.88 (m, 8 H); ^{13}C NMR δ 130.06, 128.00, 38.01, 36.88, 34.67, 31.91, 29.96, 29.45, 29.36, 29.31, 27.09, 22.68, 14.10; IR (KBr) 2976, 2957, 2918, 2872, 2849, 1464, 1440 cm^{-1}; GC/MS *m/e* 440 ($M^{\bullet+}$). Anal. Calcd for $C_{32}H_{56}$: C, 87.19; H, 12.81. Found: C, 87.21; H, 12.90.

4-Cyclohexylidenetetrahydro-4*H*-thiopyran (32(1)). Reaction of β-hydroxy acid **31** (3.22 g, 13.2 mmol) and *N,N*-dimethylformamide dineopentyl acetal (6.11 g, 26.5 mmol) in acetonitrile (160 mL) as described for **28(2)** gave a white solid which was recrystallized from acetonitrile to afford white needles (1.94 g, 10.7 mmol, 81%): mp 79–80 °C; ^1H NMR δ

2.63 (m, 4 H), 2.56 (m, 4 H), 2.16 (m, 4 H), 1.54–1.48 (m, 6 H); ^{13}C NMR δ 132.73, 126.41, 32.00, 30.91, 30.11, 28.63, 27.11; IR (KBr) 2977, 2944, 2931, 2915, 2902, 2844, 1443, 1421 cm^{-1}. Anal. Calcd for $C_{11}H_{18}S$: C, 72.47; H, 9.95. Found: C, 72.52; H, 9.98.

4-(4-Cyclohexylidenecyclohexylidene)tetrahydro-4*H*-thiopyran (32(2)). Reaction of β-hydroxy acid **36** (0.49 g, 1.51 mmol) and *N*,*N*-dimethylformamide dineopentyl acetal (0.70 g, 3.02 mmol) as described for **28(2)** afforded quantitatively a white solid: mp 175–178 °C; ^{1}H NMR δ 2.64 (m, 4 H), 2.56 (m, 4 H), 2.24 (m, 8 H), 2.17 (m, 4 H), 1.50 (m, 6 H); ^{13}C NMR δ 131.40, 130.64, 127.25, 127.13, 31.98, 30.67, 30.12, 29.26, 29.05, 28.40, 27.13; IR (KBr) 2974, 2950, 2921, 2839, 1446, 1432, 1422 cm^{-1}. Anal. Calcd for $C_{17}H_{26}S$: C, 77.79; H, 9.99. Found: C, 77.68; H, 9.94.

4-(Tetrahydro-4*H*-thiopyran-4-ylidene)cyclohexanone (35(1)). Hydrolysis of **34(1)** (3.47 g, 14.4 mmol) as described for **14(1)** afforded **35(1)** quantitatively as an off-white solid. A small amount was recrystallized from water/acetonitrile (2:3 v/v), yielding white crystals: mp 114 °C; ^{1}H NMR δ 2.63 (m, 4 H), 2.48 (m, 8 H), 2.33 (m, 4 H); ^{13}C NMR δ 212.03, 130.66, 126.40, 40.31, 32.09, 30.37, 26.26; IR (KBr) 2980, 2955, 2851, 2832, 2912, 1708, 1446, 1432, 1418, 1272 cm^{-1}. Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.12; H, 8.15.

4-(Tetrahydro-4*H*-thiopyran-4-cyclohexyliden-4′-ylidene)cyclohexanone (35(2)). Hydrolysis of **34(2)** (0.61 g, 1.90 mmol) as described for **14(1)** afforded **35(2)** quantitatively as an off-white solid: mp 183 °C; ^{1}H NMR δ 2.65 (m, 4 H), 2.53 (m, 8 H), 2.41 (m, 4 H), 2.28 (m, 8 H); ^{13}C NMR δ 212.20, 131.69, 130.34, 127.89, 124.48, 40.45, 31.99, 30.60, 29.21, 28.60, 26.49; IR (KBr) 2972, 2948, 2903, 2840, 1723, 1445, 1421 cm^{-1}.

1,1′-Bicyclohexyliden-4-ol (41(1)). To a solution of ketone **14(1)** (2.00 g, 11.2 mmol) in dioxane (100 mL) was added $NaBH_4$ (0.43 g, 11.2 mmol). Then 1 M NaOH solution (20 mL) was carefully added over a period of 15 min. After stirring at room temperature for 2 h, the mixture was acidified to pH 6 using 37% hydrochloric acid. Dioxane was removed *in vacuo*, and the resulting white slurry was dissolved in chloroform (50 mL). After washing with water, drying ($MgSO_4$), and evaporation of the solvent under reduced pressure, a white solid was isolated (1.94 g, 10.8 mmol, 96%). A small amount was recrystallized from *n*-hexane: mp 109–110 °C (lit.[12d] 115 °C); ^{1}H NMR δ 3.82 (m, 1 H), 2.59 (m, 2 H), 2.20 (m, 4 H), 1.90 (m, 4 H), 1.62–1.51 (m, 7 H), 1.32 (m, 2 H); ^{13}C NMR δ 130.91, 126.98, 70.23, 36.54, 30.31, 28.61, 27.14, 26.33; IR (KBr) 3300–3200, 2982, 2960, 2922, 2897, 2850, 2837, 1481, 1442, 1435, 1074 cm^{-1}.

Hydrogenation of Bicyclohexylidene 1(1). Bicyclohexylidene **1(1)** (1.00 g, 6.10 mmol) was dissolved in dry THF (60 mL), and 100 mg of 10% Pd on carbon was added. The mixture was stirred overnight under an atmosphere of hydrogen (atmospheric pressure, room temperature). Filtration and solvent removal gave quantitatively a colorless oil with analytical data similar to those of authentic bicyclohexyl.

Hydrogenation of Tercyclohexylidene 1(2) and Quatercyclohexylidene 1(3). A solution of 100 mg of alkene in cyclohexane containing 150 mg of 5% Rh on carbon was stirred overnight under an atmosphere of hydrogen (autoclave, 50 atm, 100 °C). For **1(2)**, filtration and solvent removal yielded quantitatively a white solid consisting of *cis*- and *trans*-tercyclohexyl in a ratio of 63:37 (GC) with correct analytical data.[20b] For **1(3)**, a white solid was isolated consisting of three isomers in a ratio of 1:2:1 having *m/e* 330 (GC/MS). The ^{13}C NMR spectrum shows only resonances due to aliphatic carbon atoms. No attempt was made to separate the isomers.

Aromatization of Bicyclohexylidene 1(1), Tercyclohexylidene 1(2), and Quatercyclohexylidene 1(3). Oligo(cyclohexylidene) **1(*n*)** was dissolved in benzene, and a slight excess of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (5.2 equiv (***n*** = 1), 7.2 equiv (***n*** = 2), and 9.2 equiv (***n*** = 3)) was added as a solid. After heating to reflux overnight, the crude reaction mixture was subjected to column chromatography (alumina; eluent, benzene). After evaporation of the solvent, a colorless solid remained which in all cases gave analytical data identical to those of authentic samples (GC/MS, ^{1}H NMR, ^{13}C NMR, IR, mp).

Aromatization of Quinquecyclohexylidene 1(4). Quinquecyclohexylidene **1(4)** (10 mg, 0.0248 mmol) was extracted with benzene in a Soxhlet apparatus until all the solid material was dissolved. The flask under the Soxhlet apparatus contained 0.56 g (2.48 mmol) of DDQ. After refluxing for 1 week, the benzene solution was washed with 5% NaOH solution, water, and brine, and after drying ($MgSO_4$), the solvent was removed at the rotary evaporator, yielding a colorless solid: GC/MS *m/e* 386 ($M^{+\cdot}$, quinquephenyl); impurity *m/e* 306 ($M^{+\cdot}$, quaterphenyl).

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Supporting Information Available: Additional synthetic schemes, synthetic procedures, and analytical data for starting materials (**6–8** and **37–40**) and intermediates (**2a**, **3a**, **4a**, **2b**, **3b**, **4b**, **2e**, **3e**, **4e**, **5e**, **2c**, **3c**, **4c**, **2f**, **3f**, **4f**, **5f**, **2d**, **3d**, **4d**, **2b-d$_4$d$_4$**, **3b-d$_4$d$_4$**, **4b-d$_4$d$_4$**, **2b-d$_8$**, **3b-d$_8$**, **4b-d$_8$**, **2g**, **3g**, **4g**, **10(1)**, **2h**, **3h**, **4h**, **2i**, **3i**, **4i**, **2j**, **3j**, **4j**, **5j**, **15(1)**, **16(1)**, **15(2)**, **16(2)**, **15(3)**, **16(3)**, **17**, **19**, **20**, **22–25**, **27**, **29**, **31**, **33(1)**, **33(2)**, **34(1)**, **34(2)**, and **36**) (20 pages). This material is contained in many 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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