DOI: 10.1002/chem.201003147

Synthesis and Ring-Opening Metathesis of Tetraalkoxy-Substituted [2.2]Paracyclophane-1,9-dienes

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Abstract: Tetraalkoxy-substituted [2.2]paracyclophane-1,9-dienes can be prepared in three steps from dithia-[3.3]paracyclophanes. A mixture of pseudo-geminal and pseudo-ortho diastereomers is produced and the pure compounds can be separated by fractional crystallization. The solid state structures of these diastereomers reveal strongly distorted aromatic rings consistent with high levels of ring strain. Reaction of these diastereomers with the second generation Grubbs catalyst shows that only the pseudo-geminal isomer can be ring opened to give *cis,trans*-distrylbenzenes. The origin of this selectivity is discussed and the photoisomerization of the as-formed *cis,-trans*-product to the all *trans* isomer is demonstrated.

Keywords: cyclophanedienes · isomers · metathesis · phenylenevinylenes · strained molecules

Introduction

Many fascinating strained molecules have been prepared over the last five decades.[1] Cyclophanes and [2.2]cyclophanes in particular have attracted tremendous attention since their discovery by Brown and Farthing in 1949.[2] Initial interest focused on the preparation, properties, and applications of [2.2]paracyclophanes[3] because of their unusually distorted π-electron system.[4,5] These molecules act as hosts for molecular guests,[6] and have been utilized in polymer chemistry and material science.[6c,7] The close approach of two coplanar benzene rings gives unique electronic properties and leads to interesting applications in areas such as chemical sensors,[8] liquid crystals,[9] and light-emitting polymers.[10]

Dewhirst and Cram introduced a double bond into each of the bridges of [2.2]paracyclophane to give the unsaturated [2.2]paracyclophane-1,9-diene.[11] This functionalization shortens the bridge, increases the interaction between the two aromatic rings, and leads to highly strained molecules. Although preparative routes to [2.2]paracyclophanes with two substituents per aromatic ring have been reported,[12] no methods to prepare the analogous tetrasubstituted [2.2]paracyclophane-1,9-dienes are available. These highly strained systems are important synthetic targets as they can be ring-opened to form soluble poly(1,4-phenylenevinylenes) by ring-opening metathesis polymerization.[13] Herein we report the preparation and solid state structures of tetraalkoxy-substituted [2.2]paracyclophane-1,9-dienes and the precursor dithia[3.3]paracyclophanes. In addition, we describe the stereospecific stoichiometric opening of the alkene bridges of the cyclophanediene by alkene metathesis.[6c,7]

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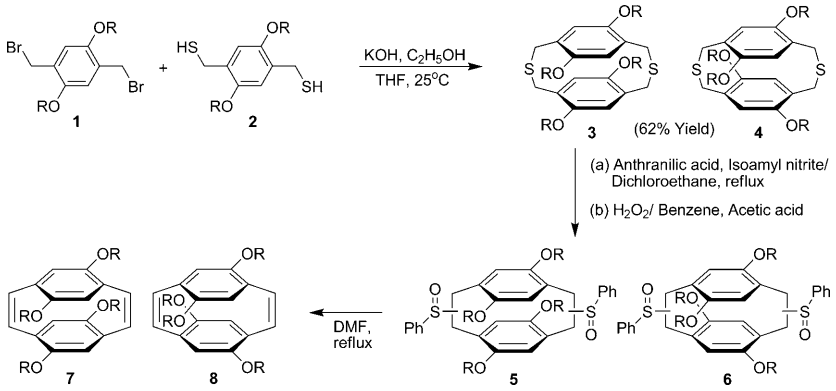
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201003147.

Results and Discussion

The synthetic route adopted is outlined in Scheme 1 and involves the initial preparation of the tetraoctyloxy-substituted dithia [3.3]paracyclophane by the condensation of **1** and **2** under pseudo high dilution conditions to avoid the formation of linear polymers.[14] A mixture of isomeric tetraoctyloxy substituted dithia[3.3]paracyclophanes, **3** and **4**, was obtained upon addition of a deoxygenated benzene solution of **1** and **2** to a deoxygenated dilute base solution at room temperature over a period of at least 60 hours. The crude mixture was purified by flash column chromatography and the desired dithia[3.3]paracyclophanes were isolated in an overall yield of 62%. Singlet signals in the ^{1}H NMR spectrum at 6.57 and 6.60 ppm were consistent with the aromatic hydrogens of the pseudo-geminal and pseudo-ortho isomers, **3** and **4**, respectively. The integration of these signals showed the presence of equimolar amounts of the two isomers.

Compounds **3** and **4** were separated by flash column chromatography with a gradient CH_2Cl_2/hexane solvent system. The ^{1}H NMR spectrum of **3** in $CDCl_3$ (Figure 1**a**) shows a singlet signal at 6.57 ppm for the aromatic hydrogens. The doublet signals at 4.48 and 3.26 ppm with $J = 15$ Hz are associated with the hydrogens of the -Ar-CH_2-S- segment. The doublet of triplets at 3.60 and 3.84 ppm with $J = 9$, 7 Hz can



Scheme 1. Preparation of tetraoctyloxy substituted [2.2]paracyclophane-1,9-dienes. R = octyl.

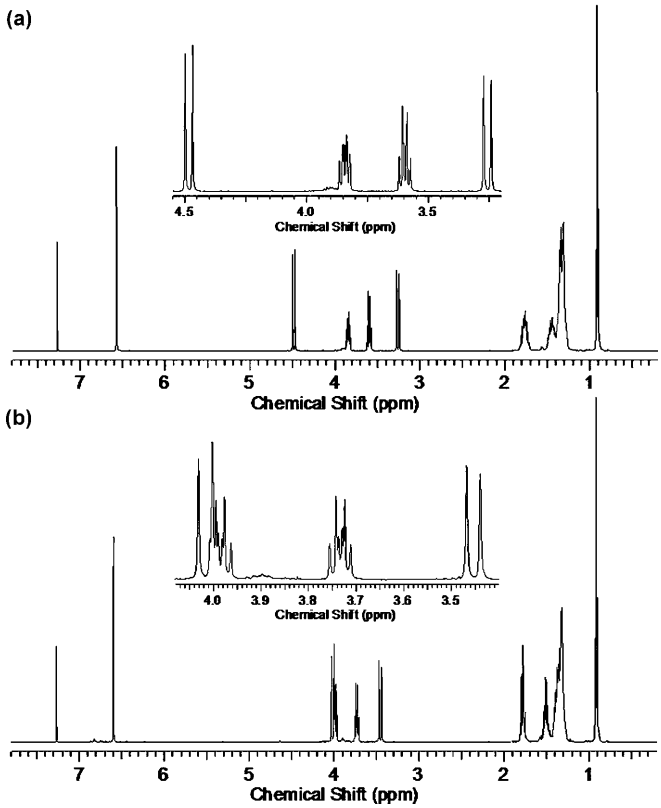


Figure 1. ^{1}H NMR spectra of **(a) 3** and **(b) 4**.

be assigned to the hydrogens of the methylene groups attached to the oxygen atom.

The two hydrogens of the methylene groups are diastereotopic as this cyclophane is planar chiral. The region below 2.00 ppm is associated with the hydrogens of the alkyl chains. The ^{1}H NMR spectrum of **4** (Figure 1**b**) shows a singlet peak at 6.60 ppm for the aromatic hydrogens. The doublet signals at 4.02 and 3.45 ppm with $J = 15$ Hz are associated with the hydrogens of the -Ar-CH_2-S- segment. The doublet of triplet signals at 3.99 and 3.73 ppm with $J = 9$, 7 Hz can be assigned to the diastereotopic hydrogens of the methylene groups attached to the oxygen atoms.

A single crystal of **3** was obtained by slow evaporation of a saturated hexane solution at room temperature. The X-ray crystal structure of **3** (Figure 2**a**) shows that the adjacent aromatic rings are parallel to one another, but not quite stacked one above the other, as there is a slippage between the two rings of 1.151 Å. The distance between the ring atoms that are connected through the bridge (C3···C6 A, symmetry equivalent A -x,1-y,-z) is significantly shorter at 3.277(2) Å than the other interatomic distances between the two aromatic rings, which are similar to one another at 3.440(2) and 3.390(2) Å for C5···C8 A and C4···C7 A, respectively (symmetry equivalent A -x,1-y,-z). This is because the two aromatic rings are slightly distorted and nonplanar, with the atom C3 and C6 lying 0.073(2) Å above the least squares plane through the atoms C4, C5, C7, and C8. Similar characteristics are seen in the unsubstituted dithia-[3.3]paracyclophane molecule,[15] except that the aromatic rings are nearly eclipsed with a slippage of only 0.252 Å. The average C(aryl)–C(methylene) bond length (1.510(2) Å) is comparable to that in toluene. The C-S-C angle of 102.09(9)° is slightly smaller than that in unsubstituted dithia [3.3]paracyclophane of 103.9(1)°.[15]

A single crystal of **4** was obtained by slow evaporation of a saturated hexane solution at room temperature. The X-ray crystal structure of **4** (Figure 2**b**) shows that the aromatic rings are slightly inclined to one another at an angle of 13.8(1)°. The interatomic separations between the ring atoms connected via the bridges (i.e. C4···C9 and C1···C12) are 3.274(2) and 3.283(2) Å, respectively. Because of the angle of tilt between the two rings, the interatomic distances between the ring atoms on one side of the bridges are considerably shorter at 3.102(2) and 3.130(2) Å (C5···C14 and C6···C13) than those on the other side (i.e. 3.687(2) and 3.688(2) Å for C2···C11 and C3···C10, respectively). The average C(aryl)–C(methylene) bond length (1.507(1) Å) is comparable to that in toluene. The C-S-C angles are 103.51(8) and 103.54(8)°, and slightly larger than for **3**.

The solid state structures of **3** and **4** show that the bridges of the thiacyclophanes adopt different conformations. The bridges of **3** adopt the chair conformation and those of **4** the boat conformation; in **4**, the boat conformation leads to the tilting of the aromatic rings described in the previous paragraph, which are closer together on the side of the bridge away from the sulfur atoms. These conformations are also present in solution as the ^{1}H NMR spectrum of **3** shows a large difference in chemical shift (1.2 ppm) between the two hydrogens of the methylene groups in the bridge, which is characteristic of the chair conformation; conversely, that of **4** shows a much smaller separation (0.6 ppm), which is char-

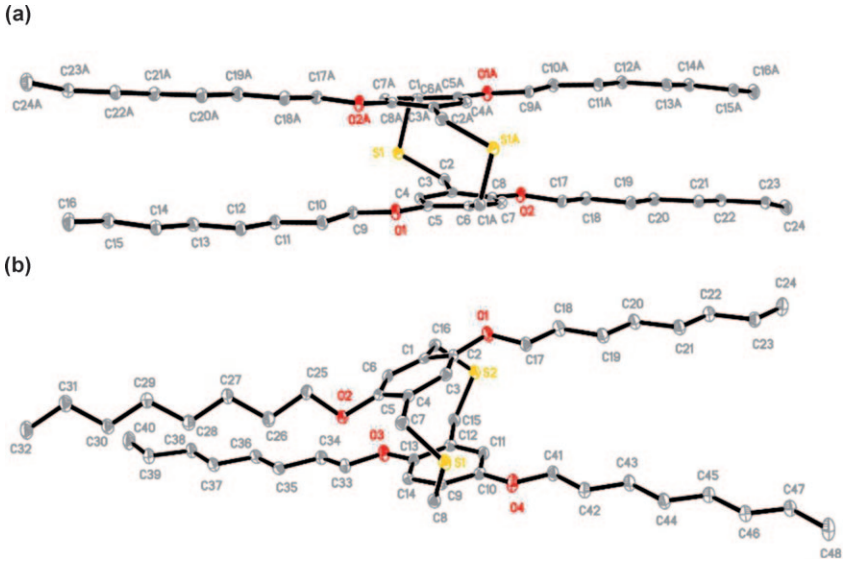


Figure 2. Solid-state structure of **(a) 3** and **(b) 4**. Thermal ellipsoids are set at 50% probability.

acteristic of the boat conformation. Both conformations have previously been identified for related unsubstituted and substituted thia[3.3]cyclophanes.[15–17] The conformational preferences adopted by **3** and **4** appear to be determined by the steric influence of the alkoxy substituents, as the sulfur atoms in the bridge of the pseudo-geminal isomer point away from these groups in the observed chair conformation.[17]

A number of synthetic methods have been identified that lead to ring contraction by a sulfur-mediated rearrangement reaction.[18] These reactions were screened for the conversion of **3** and **4** into the desired cyclophanedienes **7** and **8**. Initially, the Ramberg–Bäcklund reaction was attempted to convert the sulfide linkage through a sulfone to produce the desired carbon–carbon double bond.[18a,b] However, this reaction failed primarily due to difficulty with the halogenation step. The conversion of dithia[3.3]cyclophanes into [2.2]cyclophanedienes may also be achieved by a Stevens rearrangement followed by a Hofmann elimination.[18c] The Stevens rearrangement of either **3** or **4** with dimethoxymethyliumtetrafluoroborate in CH_2Cl_2 followed by treatment with potassium *tert*-butoxide or sodium hydride in THF gave a large mixture of products resulting from many competing side reactions.[19,20] The scope of the method has been extended by the discovery of the Wittig modification that improves the yield of this reaction.[18d] Unfortunately, when using this approach the paracyclophane derivatives underwent side reactions and only gave the desired [2.2]paracyclophanes in very poor yield. Otsubo and Boekelheide reported that the Stevens rearrangement of dithia[3.3]cyclophanes can be achieved by the generation of benzyne in situ followed by oxidation and pyrolysis of the resulting sulfoxides.[19] The reaction of **3** and **4** with benzyne generated in situ by the reaction of anthranilic acid and isoamyl nitrite under reflux of dry 1,2-dichloroethane gave the desired rearrangement products in a total of 31% yield. The product is a mixture of numerous potential isomers and efforts to separate these isomers by column chromatography and high performance liquid chromatography with reversed or normal phase silica gel failed due to the very similar polarity of the isomers. The NMR spectra of this complex mixture of isomers contained a very large number of overlapping signals (see the Supporting Information). The mass spectrum shows a molecular ion at the correct mass of 936 $[M]^+$ and high-resolution mass spectrometry gave a molecular ion of 936.6100 (calculated for $[M]^+$: 936.6119).

In general, the oxidation of aliphatic sulfides can be achieved using *m*-chloroperbenzoic acid (*m*CPBA) in chloroform at room temperature.[21] However, the oxidation of the products derived from the rearrangement reaction under these conditions was unsuccessful and the starting material was recovered. Room temperature oxidation using a 30% w/w solution of hydrogen peroxide in a 1:3 ratio of acetic acid/benzene was successful and the desired bis-sulfoxide isomers **5** and **6** were obtained in an overall yield of 90% after a simple extraction and column chromatography. Characterization by NMR spectroscopy was very difficult due to a very large number of isomers of **5** and **6**. The mass spectrum of the mixture shows a molecular ion at the correct mass of 992 $[M+Na]^+$. This is further confirmed by high-resolution mass spectrometry that gives a molecular ion of 991.5912 (calcd for $[M+Na]^+$: 991.5915).

Kingsbury and Cram first reported the thermal elimination of sulfenic acid from a sulfoxide to generate an alkene.[22] Thermal elimination of sulfenic acid[23] can be achieved either by heating in a high boiling point solvent or under vacuum in a gradient sublimation apparatus. The former method always gives a higher yield than the latter. Therefore, the mixture of **5** and **6** was heated to reflux in *N*,*N*-dimethylformamide (DMF) with a nitrogen purge for 20 hours to give the desired paracyclophanedienes, **7** and **8** in an overall yield of 25%. High-resolution mass spectrometry gave a molecular ion of 716.5722 (calcd for $[M]^+$: 716.5738). Separation of the two isomers, **7** and **8**, was achieved by fractional crystallization in hexane at 5°C and −10°C, to give an isolated yield of 11% of **7** and 14% of **8**, respectively.

The ^{1}H NMR spectrum of **7** (Figure 3**a**) shows singlet signals at 6.92 and 5.85 ppm for the alkene and aromatic hydrogens, respectively. The unusual upfield shift of the aromatic hydrogens can be explained by the influence of the aromatic ring current. The doublet of triplet signals at 3.82 and 3.73 ppm (ABX_2 system with $J=9$, 7 Hz) can be as-

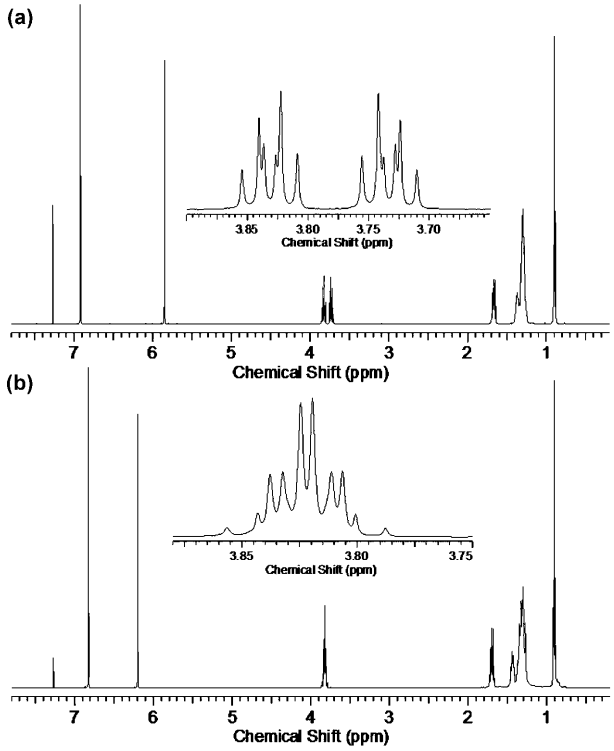


Figure 3. ^{1}H NMR spectra of **(a) 7** and **(b) 8**.

signed to the hydrogens of the methylene groups attached to the oxygen. These hydrogens are diastereotopic due to the planar chirality of the cyclophanedienes. The region below 2.00 ppm is associated with the hydrogens of the alkyl chain. The ^{1}H NMR spectrum of **8** (Figure 3**b**) shows singlet peaks at 6.83 and 6.20 ppm, which correspond to the alkene and aromatic hydrogens, respectively. The signal at around 3.8 ppm can be assigned to the methylene groups attached to the oxygen and was analyzed as an ABX_2 system composed of two sets of doublet of triplets at 3.83 and 3.82 ppm with $J=9$, 7 Hz. Again, the region below 2.00 ppm is associated with the hydrogens of the alkyl chains.

A single crystal of **7** was obtained by fractional crystallization of the mixtures of **7** and **8** in a saturated hexane solution at 5 °C. The crystallization procedure was repeated three times to obtain a high quality, transparent single crystal of **7**. The X-ray crystal structure of **7** (Figure 4**a**) shows that the interatomic distance between the atoms of the adjacent rings that are connected through the bridge (i.e. C2···C5 A, symmetry equivalent A $1-x$,-y,2-z) is only 2.781(2) Å. The other ring atoms are significantly further apart, with intra-ring distances between the carbon atoms with or without the alkoxy groups (i.e. C1···C4 A and C3···C6 A, symmetry equivalent A $1-x$,-y,2-z) of 3.151(2) and 3.070(2) Å, respectively. However, all these distances are considerably shorter than the normal separation between parallel aromatic rings of about 3.4 Å, or more, but they are comparable to the corresponding values in unsubstituted [2.2]paracyclophane-1,9-diene of 2.790(1), 3.124(1) and 3.122(1) Å, respectively.[24] This shortening leads to a considerable transannular π–π overlap. Moreover, the aromatic rings of **7** are forced to be nonplanar, with the atoms C2 and C5 lying 0.165(2) Å below the least squares plane through the atoms C1, C3, C4, and C6. The corresponding distances of the bridging aromatic ring atoms out of the plane through the central atoms of the rings in unsubstituted [2.2]paracyclophane-1,9-diene are very similar (0.1666(9) and 0.1662(9) Å). The alkene bond length of 1.331(2) Å is normal (1.33 Å) and the average C(aryl)–C(methine) bond length of 1.499(2) Å is comparable to that in toluene. The C-(aryl)-C(methine)-C(methine) angles of 118.7(1)° and 119.1(1)° are in agreement with those in [2.2]paracyclophane-1,9-diene (118.53(9)° and 118.89(9)°) reported previously.[11,25]

A single crystal of **8** was obtained by fractional crystallization in a saturated hexane solution at −10 °C. The crystallization procedure was repeated three times to obtain a high quality, transparent single crystal of **8**. The X-ray crystal structure of **8** (Figure 4**b**) shows similar characteristics to that of **7**. In particular, the distances between the bridging carbon atoms of two aromatic rings are 2.763(2) and 2.790(2) Å, and the intramolecular separations between the central ring carbon atoms are 3.070(2), 3.075(2), 3.100(2), and 3.129(2) Å. Also, the aromatic rings are slightly boat shaped, with the atoms C2 and C5 0.160(1) and 0.172(1) Å above the least squares plane through the atoms C1, C3, C4,

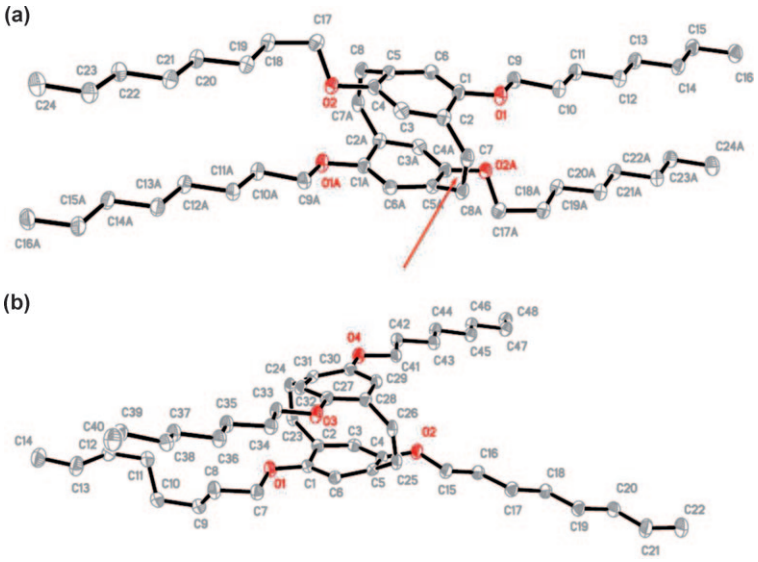
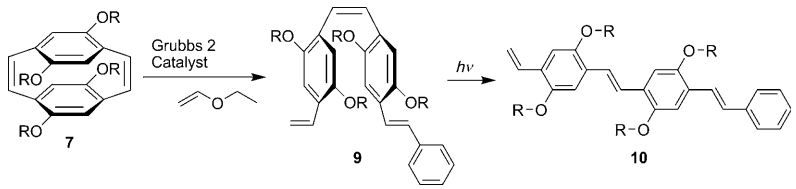


Figure 4. Solid-state structure of **(a) 7** and **(b) 8**. Thermal ellipsoids are set at 50% probability.

C6, and the atoms C28 and C31 0.150(1) and 0.156(1) Å below the least squares plane through the atoms C27, C29, C30, C32. Other geometric parameters are similar to those in **7**.

The strain energy of [2.2]paracyclophane-1,9-diene has been experimentally determined to be higher than 40 kcal mol^{-1}.[25] The similarity of the geometric parameters of **7** and **8** to the parent unsubstituted cyclophanediene suggests that **7** and **8** are highly strained and that they should be good substrates for ring-opening metathesis. The reaction of **7** (Scheme 2) with a stoichiometric amount of the second



Scheme 2. Ring-opening metathesis reaction of **7** and photoisomerization of **9**. R = octyl.

generation Grubbs' catalyst proceeded smoothly in [D$_8$]THF at 55 °C with complete consumption of **7** after 6 hours. This was shown by the disappearance of the signals at 6.92 and 5.85 ppm in the ^{1}H NMR spectrum that are associated with the alkene and aromatic hydrogens of **7**. Surprisingly, the same reaction of the Grubbs' second generation catalyst with **8** showed no evidence for reaction even after heating for 12 hours at 55 °C, indicating that the ring-opening metathesis reaction of **8** did not proceed. A plausible explanation for this observation is that the alkoxy substituents of the aromatic rings shield both faces of the alkene bridges and hence the catalyst is unable to form the π complex with **8**. By comparison in compound **7**, one face of the alkene (indicated with an arrow in Figure 4) is able to coordinate to the ruthenium complex, thereby leading to the formation of the required metallacyclobutane intermediate by a stereospecific ring opening metathesis reaction.

The ring-opened product **9** was isolated by treatment of the initially formed ruthenium carbene complex with ethyl vinyl ether. The ^{1}H NMR spectrum of **9** (Figure 5**a**) recorded in CD_2Cl_2 shows four major triplet signals at 4.00, 3.96 ppm (J = 7 Hz), and 3.58, 3.55 ppm (J = 7 Hz) corresponding to the hydrogens of the methylene groups attached to the oxygen for the *trans*- and *cis*-alkenes, respectively. Integration of these signals gave the expected 1:1 ratio of *cis*- and *trans*-alkenes, consistent with the release of ring strain by the opening of only one alkene bridge. The signals for the vinyl group are observed as a doublet of doublet at 5.24 ppm (J = 11 Hz, 2 Hz), a doublet of doublet at 5.72 ppm (J = 18 Hz, 2 Hz), and a doublet of doublet at 6.98 ppm (J = 18 Hz, 11 Hz). The signal for the *cis*-vinylene hydrogens appears at 6.75 ppm. Doublet signals at 7.42 and 7.12 ppm with J = 17 Hz are assigned to the *trans*-vinylene hydrogens. The signals for phenyl end groups appear as a triplet at 7.34 ppm (J = 8 Hz) for the *m*-phenyl hydrogens, a triplet at 7.24 ppm (J = 8 Hz) for *p*-phenyl hydrogen, and a doublet at 7.51 ppm (J = 8 Hz) for *o*-phenyl hydrogens. Singlet peaks at 7.11, 7.00, 6.76, and 6.75 ppm are assigned to the other aromatic hydrogens.

Isomerization of **9** to the *trans*-alkene **10** was possible in CD_2Cl_2 by exposure to sunlight. However, the reaction does not go to completion even after exposure to sunlight in Manchester (UK) for one week. Rapid photoisomerization can be achieved using an 8W UV lamp at a wavelength of 365 nm. The *trans* compound **10** was obtained after purification by flash column chromatography in 69% yield. The ^{1}H NMR spectrum of **10** (Figure 5**b**) in $CDCl_3$ shows four triplet signals at 4.06, 4.06, 4.02, and 4.02 ppm (J = 7 Hz), these can be assigned to the hydrogens of the methylene groups attached to the oxygen for the *trans*-vinylene links. The signals for the vinyl end groups appear as a doublet of doublet at 5.27 ppm (J = 11 Hz, 1 Hz), a doublet of doublet at 5.76 ppm (J = 18 Hz, 1 Hz), and a doublet of doublet at 7.08 ppm (J = 18 Hz, 11 Hz). The hydrogens of the *trans*-vinylene between the substituted phenyl-

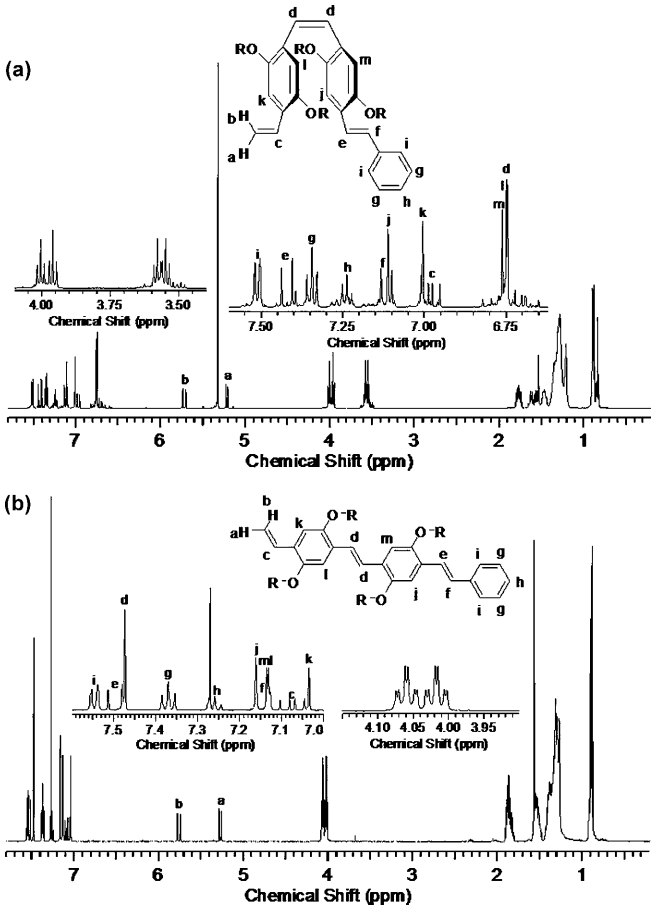


Figure 5. ^{1}H NMR spectra of **(a) 9** and **(b) 10**.

ene units appear as a singlet at 7.47 ppm due to the similarity of the adjacent groups. *Trans*-vinylene hydrogens next to the phenyl end group appear at 7.50 ppm and 7.15 ppm as doublet signals with $J=17$ Hz, respectively. The signals for the phenyl end group appear as a triplet at 7.37 ppm ($J=$ 8 Hz) for the *m*-phenyl hydrogens, a triplet at 7.26 ppm ($J=$ 8 Hz) for *p*-phenyl hydrogen, and a doublet at 7.54 ppm ($J=$ 8 Hz) for *o*-phenyl hydrogens. The other aromatic hydrogens appear as singlets at 7.16, 7.14, 7.13, and 7.03 ppm (Table 1).

Table 1. Crystallographic details for the crystal structures of **3**, **4**, **7**, and **8**.

	3	**4**	**7**	**8**
formula	$C_{48}H_{80}O_4S_2$	$C_{48}H_{80}O_4S_2$	$C_{48}H_{76}O_4$	$C_{48}H_{76}O_4$
M_r	785.24	785.24	717.09	717.09
dimensions[mm3]	$0.65\times0.35\times0.20$	$0.50\times0.30\times0.25$	$0.40\times0.30\times0.25$	$0.50\times0.50\times0.30$
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.299(5)	16.169(1)	8.5200(10)	9.2527(5)
b [Å]	9.424(5)	18.417(1)	9.0864(11)	16.148(1)
c [Å]	12.946(5)	16.377(1)	14.1204(17)	16.509(1)
α [°]	91.716(5)	90	75.987(2)	116.219(1)
β [°]	93.743(5)	111.924(2)	84.823(2)	90.127(1)
γ [°]	100.942(5)	90	82.520(2)	102.792(1)
V [Å^3]	1110.5(9)	4524.1(6)	1049.6(2)	2143.7(2)
Z	1	4	1	2
ρ_{calad} [mgcm^{-3}]	1.174	1.153	1.134	1.111
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.162	0.159	0.069	0.068
F(000)	432	1728	396	792
meas. reflections	8780	28087	6042	16906
unique reflections	4457	10613	4172	8609
obs. refl. [$I_0>2\sigma(I_0)$]	4142	6236	2656	6238
goodness of fit on F^2	1.242	0.820	0.906	1.017
R_1	0.0433	0.0454	0.0433	0.03949
wR_2	0.1546	0.0825	0.0921	0.1033
R_1 (all data)	0.0456	0.0825	0.0727	0.0577
wR_2 (all data)	0.1559	0.0903	0.1003	0.1093

Conclusion

Tetraalkoxy-substituted [2.2]paracyclophane-1,9-dienes can be synthesized in three steps from dithia-[3.3]paracyclophanes. Two diastereomers (**7** and **8**) were isolated by fractional recrystallization, and X-ray crystallography showed that these compounds have highly distorted aromatic ring systems consistent with a large ring strain. Surprisingly, only the pseudo-geminal isomer, **7**, can be ring opened by a stoichiometric amount of second generation Grubbs' catalyst to give the linear *cis,trans*-distrylbenzene **9**. This compound can be photoisomerized to the all *trans* isomer **10**. Substituted [2.2]paracyclophanedienes are extremely attractive precursors for well-defined, soluble poly(1,4-phenylenevinylene) by ring opening metathesis polymerization. Further work is in progress to demonstrate the synthetic utility of this approach to synthesize a wide range of symmetric and asymmetric [2.2]cyclophanedienes.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded in deuterated chloroform with chemical shifts referenced to residual chloroform as an internal standard on a Bruker Ultrashield 500 MHz spectrometer. GC-MS analysis was performed using a HP 5890 Series II GC connected to a HP5971 A mass spectrometer (EI). APCI mass spectra were recorded on a Micromass Trio 2000 spectrometer. MALDI-TOF mass spectra were obtained on a Micromass TOF Spec 2E instrument using dithranol as the matrix. 1,2-Dichloroethane was distilled under nitrogen from calcium hydride. Unless otherwise noted, all reagents were used as received from commercial suppliers without further purification. Melting points were measured by polarized optical microscopy on an Olympus BH2 microscope attached to a temperature controller module Linkam TMS 94 hot stage and are uncorrected. The compounds, 2,5-bis(bromomethyl)-1,4-dioctyloxybenzene (**1**) and 2,5-bis(thiolatomethyl)-1,4-dioctyloxybenzene (**2**) were synthesized by a modification of established procedures.[18c,26]

X-ray crystallographic data for single crystals were determined using a Bruker Smart APEX CCD diffractometer equipped with an Oxford Cryosystems 700 series cryostream cooler using graphite monochromated MoKα radiation. CCDC-755376 (**7**), 755377 (**8**), 755378 (**3**), and 755379 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 5,8,14,17-tetraoctyloxy-2,11-dithia[3.3]paracyclophane (**3**) and 6,9,14,17-tetraoctyloxy-2,11-dithia-[3.3]paracyclophane (**4**) A deoxygenated solution of **1** (14.56 g, 28 mmol) and **2** (11.93 g, 28 mmol) in benzene (600 mL) was added dropwise to a deoxygenated solution of KOH (3.92 g, 70 mmol) in ethanol (900 mL) under a nitrogen atmosphere for a period of at least 60 h. After further 2 h, the solvent was evaporated and the residue was extracted with aqueous HCl and dichloromethane. The organic layers were combined, washed with water, dried with $MgSO_4$, and the solvents evaporated. The resulting yellow solid was dissolved in a solvent system of 20% CH_2Cl_2 and 80% hexane and purified by flash chromatography. Collection of the main fraction gave a mixture of **3** and **4** as a white solid in 62% yield. Further separation of the two isomers was possible by flash chromatography using a gradient CH_2Cl_2/hexane solvent system.

3: m.p. 86–87 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=6.57$ (s, 4H), 4.48 (d, $J=15.3$ Hz, 4H), 3.84 (dt, $J=8.7$, 7.1 Hz, 4H), 3.60 (dt, $J=8.7$, 7.1 Hz, 4H), 3.26 (d, $J=15.3$ Hz, 4H), 1.72–1.82 (m, 8H), 1.26–1.52 (m, 40H), 0.91 ppm (t, $J=7.0$ Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=150.52$, 125.20, 113.72, 68.80, 31.89, 30.73, 29.69, 29.60, 29.35, 26.26, 22.69, 14.12 ppm; MS (EI): *m/z* (%): 785 $[M+H]^+$; HRMS (EI); *m/z* (%) calcd for $[M]^+$: 784.5493; found: 784.5493.

4: m.p. 51–52 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=$ 6.60 (s, 4H), 4.02 (d, $J=14.6$ Hz, 4H), 3.99 (dt, $J=9.0$, 6.5 Hz, 4H), 3.73 (dt, $J=9.0$, 6.5 Hz, 4H), 3.45 (d, $J=14.6$ Hz, 4H), 1.74–1.82 (m, 8H), 1.26–1.56 (m, 40H), 0.91 ppm (t, $J=7.0$ Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta=150.00$, 125.02, 114.67, 68.89, 31.89, 29.73, 29.54, 29.34, 26.36, 22.70, 14.12 ppm; MS (EI): *m/z*: 785 $[M+H]^+$; HRMS (EI): *m/z* calcd for $[M]^+$: 784.5485; found 784.5493.

Synthesis of 4,7,12,15-tetraoctyloxy-[2.2]paracyclophane-1,9-diene (**7**) and 5,8,12,15-tetraoctyloxy-[2.2]paracyclophane-1,9-diene (**8**) A solution of **5** and **6** (4.36 g, 4.5 mmol) in *N,N*-dimethylformamide (300 mL) was heated at reflux under a nitrogen stream for 20 h. The solution was cooled to room temperature and extracted successively with aliquots of dilute aqueous HCl and CH_2Cl_2, dried with $MgSO_4$, and concentrated to give a pale yellow oil. The resulting oil was then subjected to flash chromatography over silica gel using CH_2Cl_2/hexane (1:4) as the eluent. The isolated mixture was then further purified by fractional recrystallization at 5 °C

and −10 °C in saturated hexane to give **7** in 11% yield and **8** in 14% yield.

7: m.p. 69–70 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.92$ (s, 4H), 5.85 (s, 4H), 3.82 (dt (ABX_2), $J = 8.9$, 6.8 Hz, 4H), 3.73 (dt (ABX_2), $J = 8.9$, 6.8 Hz, 4H), 1.63–1.71 (m, 8H), 1.25–1.40 (m, 40H), 0.89 ppm (t, $J = 7.0$ Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 152.78$, 133.39, 126.10, 119.57, 69.91, 31.86, 29.78, 29.55, 29.31, 26.06, 22.68, 14.11 ppm; MS (EI): m/z: 717 $[M+H]^+$; HRMS (EI): m/z calcd for $[M]^+$: 716.5738; found: 716.5722.

8: m.p. 28–29 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.83$ (s, 4H), 6.20 (s, 4H), 3.83 (dt (ABX_2), $J = 9.3$, 6.7 Hz, 4H), 3.82 (dt (ABX_2), $J = 9.3$, 6.7 Hz, 4H), 1.66–1.74 (m, 8H), 1.25–1.49 (m, 40H), 0.91 ppm (t, $J = 7.0$ Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 153.35$, 132.83, 128.15, 117.33, 69.35, 31.68, 29.65, 29.40, 29.33, 26.20, 22.68, 14.11 ppm; MS (EI): m/z: 717 $[M+H]^+$; HRMS (EI): m/z calcd for $[M]^+$: 716.5738; found: 716.5722.

Preparation of compound 9 Compound **7** (28.6 mg, 0.04 mmol) and the second generation Grubbs' catalyst (40.8 mg, 0.048 mmol) were charged into a glass NMR tube and dissolved in 1.2 mL of degassed, deuterated THF. The mixture was sonicated for at least 10 min at room temperature to ensure complete dissolution of the reagents. The mixture was then heated at 55 °C in an oil bath and periodically monitored by NMR spectroscopy. Complete reaction of **7** was observed after 6 h and the reaction mixture was then cooled to room temperature and poured into a large excess of degassed ethyl vinyl ether (4 mL) to quench the reaction. After stirring for a further 2 h at room temperature, the reaction mixture was concentrated in vacuo. The products were redissolved in CH_2Cl_2/hexane (1:1) and filtered through a short plug of silica to remove the ruthenium complex and any phenylenvinylene oligomers. The solvent was removed under reduced pressure to yield an orange oil (18 mg) in 62% yield.

9: ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 7.51$ (d, $J = 7.7$ Hz, 2H), 7.42 (d, $J = 16.5$ Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.24 (t, $J = 7.7$ Hz, 1H), 7.12 (d, $J = 16.5$ Hz, 1H), 7.11 (s, 1H), 7.00 (s, 1H), 6.98 (dd, $J = 17.7$, 11.1 Hz, 1H), 6.76 (s, 1H), 6.75 (s, 1H), 6.75 (s, 2H), 5.72 (d, $J = 17.7$, 1.5 Hz, 1H), 5.24 (dd, $J = 11.1$, 1.5 Hz, 1H), 4.00 (t, $J = 6.6$ Hz, 2H), 3.96 (t, $J = 6.6$ Hz, 2H), 3.58 (t, $J = 6.6$ Hz, 2H), 3.55 (t, $J = 6.6$ Hz, 2H), 1.81–1.73 (m, 4H), 1.65–1.53 (m, 4H), 1.51–1.17 (m, 40H), 0.95–0.80 ppm (m, 12H); MS (APCI): m/z: 821 $[M+H]^+$.

Photoisomerization of **9** was carried out in a solution in CH_2Cl_2 using an 8W UV lamp (wavelength: 365 nm). The all trans-isomer, **10**, was isolated by flash column chromatography using CH_2Cl_2/hexane (1:4) as eluent in 69% yield.

10: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.54$ (d, $J = 7.7$ Hz, 2H), 7.50 (d, $J = 16.5$ Hz, 1H), 7.47 (s, 2H), 7.37 (t, $J = 7.7$ Hz, 2H), 7.26 (t, $J = 7.7$ Hz, 1H), 7.15 (d, $J = 16.5$ Hz, 1H), 7.16 (s, 1H), 7.14 (s, 1H), 7.13 (s, 1H), 7.08 (dd, $J = 17.8$, 11.2 Hz, 1H), 7.03 (s, 1H), 5.76 (dd, $J = 17.8$,1.4 Hz, 1H), 5.27 (dd, $J = 11.2$, 1.4 Hz, 1H), 4.06 (t, $J = 6.5$ Hz, 2H), 4.06 (t, $J = 6.5$ Hz, 2H), 4.02 (t, $J = 6.5$ Hz, 2H), 4.02 (t, $J = 6.5$ Hz, 2H), 1.90–1.80 (m, 8H), 1.58–1.19 (m, 40H), 0.94–0.85 ppm (m, 12H); MS (APCI): m/z: 821 $[M+H]^+$.

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Received: November 2, 2010
Published online: May 5, 2011

