Synthesis and Properties of Trispiro[truxenetris(cycloalkane)]s

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Four of the title compounds, where cyclopropane, cyclobutane, cyclopentane, and cyclohexane rings are spiro-annelated at the 5-, 10-, and 15-positions of truxene, were synthesized and their spectral properties were studied. X-ray molecular structures were elucidated for the cyclopropane compound.

Truxene (**1**), 10,15-dihydro-5*H*-diindeno[1,2-*a*:1′,2′-*c*]fluorene by the IUPAC nomenclature, has a unique structure with a planar C_{3h} framework, and has drawn much attention because of the acidity of the methylene moieties (5-, 10-, and 15-positions) and the potential derivatization at these positions affording various interesting molecules in the fields of structural organic chemistry and supramolecular chemistry.[1] We have been interested in the chemistry of compounds in which three cyclic moieties are spiro-annelated to the methylene groups of truxene. We started with trispiro[truxene-5,1′:10,1″:15,1‴-tris(cycloalkane)]s **2**, where three cycloalkane moieties are spiro-annelated at the 5-, 10-, and 15-positions of truxene. In these molecules, σ–π interactions are expected through the spiro moieties and elucidation of these interactions and the effects on their structures and properties are of interest. The concept of spiroconjugation has been put forward by Simmons and Fukunaga,[2] and by Hoffmann et al.,[3] the effects of spiroconjugation have been proven theoretically[4] and experimentally.[5]

In this article, we report the synthesis of compounds **2a**–**2d** (Chart 1) and their structural, spectral, and electronic properties.

Results and Discussion

Syntheses. At first, we tried to prepare **2** according to the literature method for the preparation of spiro[cycloalkanefluorene]s, which employed a one-step procedure in which fluorene was treated with 2 equiv of a base and then with 1,ω-dibromoalkane, to afford directly the final product.[6] However, the yields were rather low because of the intervention of intermolecular reactions, especially when the alkyl chain was long. We therefore employed a two-step procedure.

Truxene (**1**) was treated with 3 equiv of butyllithium to give the corresponding trianionic species, which was then treated with 3.3 equiv of 1,ω-dibromoalkane to afford the corresponding 5,10,15-tris(ω-bromoalkyl)truxene **3** as a mixture of two stereoisomers, *syn* and *anti*. The *syn*–*anti* ratio was ca. 1:3 in any of the compounds as revealed by ^{1}H NMR. Treatment of **3** with KH in THF caused cyclization to give the respective trispiro compound **2** (Scheme 1).

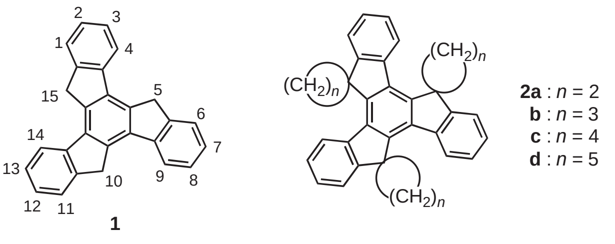
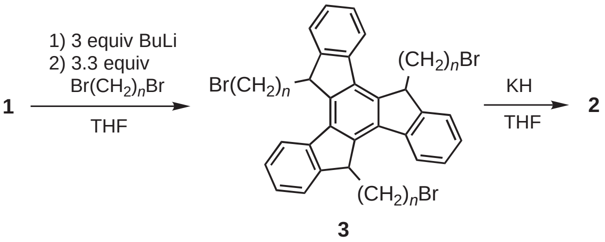


Chart 1.



Scheme 1.

X-ray Crystallography. Since single crystals suitable for X-ray diffraction were obtained for **2a**, X-ray crystallographic analysis was performed. The crystal of **2a** contained two crystallographically independent molecules, **A** and **B**, which differ in the planarity of the truxene moiety (Fig. 1). The truxene ring of molecule **A** was deformed to a concave–convex form, while that in **B** was nearly planar. The plane of each cyclopropane ring lies perpendicular to the mean plane of the spiro-

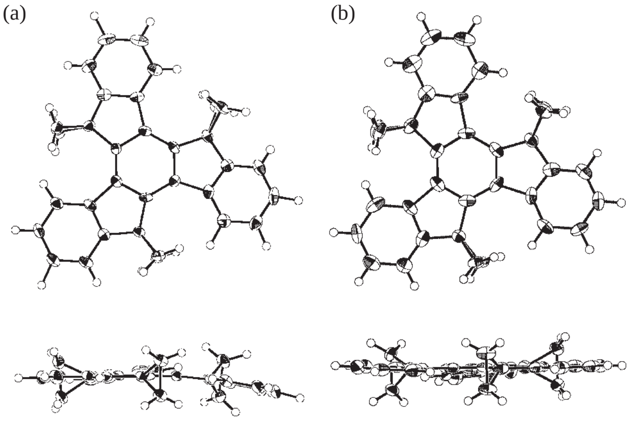
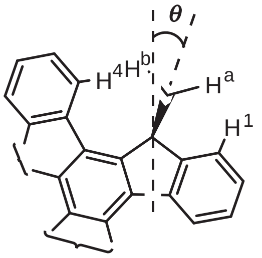


Fig. 1. Molecular structures of two independent molecules of **2a**, (a) molecule **A**, and (b) molecule **B** (ellipsoids at the 50% probability level).

Published on the web June 6, 2006; doi:10.1246/bcsj.79.938



Scheme 2.

Table 1. Selected Structural Parameters for Molecules **A** and **B** of **2a**[a)]

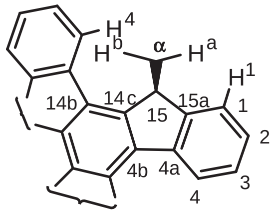
Molecule	**A**	**B**
C^{sp}–C^{α}	1.521(4), 1.510(4)	1.538(4), 1.545(4)
	1.531(4), 1.526(4)	1.546(5), 1.529(4)
	1.532(4), 1.519(4)	1.544(4), 1.543(4)
average	1.528	1.543
C^{α}–C^{α}	1.491(4)	1.509(4)
	1.509(4)	1.506(4)
	1.500(4)	1.504(4)
average	1.500	1.506
C^{α}–C^{sp}–C^{α}	58.9(2)	58.6(2)
	59.2(2)	58.6(2)
	58.9(2)	58.3(2)
average	59.0	58.5
C^{Ar}–C^{sp}–C^{Ar}	105.9(2)	107.3(3)
	105.8(2)	107.5(3)
	105.5(2)	107.0(3)
average	105.7	107.3
Tilt angle θ[b)]	3.1, 3.9, 4.9	3.8, 4.0, 4.9
average	4.0	4.2

a) Bond lengths are given in Å, and angles in °. b) See Scheme 2.

annelated five-membered ring of the truxene moiety and slightly tilts at angles of 3.1 to 4.9°, presumably due to the steric repulsion with the flanking benzene ring (Scheme 2). This feature is consistent with the low-field shifts of H^4 and H^b, and the large NOE effect among them in the ^{1}H NMR spectrum as described later.

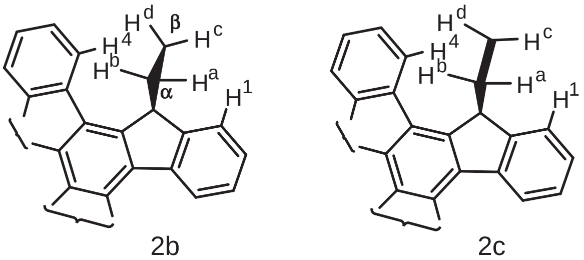
Selected structural parameters around the spiro moieties for both molecules are listed in Table 1. The C^{sp}–C^{α} bond lengths (sp refers to a spiro carbon) are in the range of 1.51 to 1.55 Å in both molecules, and are larger than the C^{α}–C^{α} ones (1.49 to 1.51 Å). The C^{α}–C^{sp}–C^{α} angles are slightly smaller than 60°. These features are almost completely coincident with those found in spiro[cyclopropane-1,9′-fluorene] (**5a**),[7] and are generally observed for cyclopropane derivatives with an electron-accepting group as a substituent; these are ascribed to the σ–π orbital interactions between the σ orbital at the ring juncture of the cyclopropyl group and the neighboring π orbital.[8]

^{1}H NMR Spectra. The ^{1}H NMR spectra of the compounds examined consisted of the aromatic ABCD four-spin signals and aliphatic signals, and were analyzed with the aid of decoupling and nuclear Overhauser effect (NOE) experiments. The chemical shift data are compiled in Table 2. In the cyclopropane derivative **2a**, for example, the aliphatic protons appear at δ 1.70 and 2.99 as AA′BB′ multiplets. Irradiation of the lowest-field aromatic signal at δ 8.09 enhanced the aliphatic signal at δ 2.99 by ca. 20% due to NOE, while irradiation of the highest-field aromatic signal at δ 7.05 enhanced the δ 1.70 signal by ca. 10%. Thus, the former pair was assigned to H^4 and H^b, which are most closely located to each other by the molecular structures determined above, while the latter pair was assigned to H^1 and H^a, which are also proximate (Scheme 3).



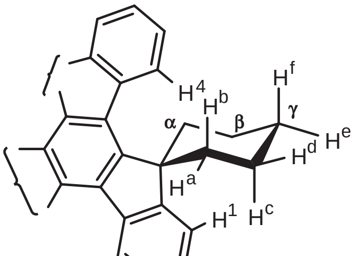
2a

Scheme 3.



2b 2c

Scheme 4.



2d

Scheme 5.

The spectra of **2b**–**2d** were similarly analyzed and assigned (Table 2). In **2b**, irradiation of H^4 at δ 8.48 enhanced the H^b (δ 3.66, 15%) and H^d (δ 2.68, 10%) signals, while irradiation of H^1 at δ 8.10 enhanced the H^a (δ 2.44, 4%) and H^c (δ 2.91, 5%) signals (Scheme 4). In **2c**, similarly, the proximity of H^4 to H^b and H^d, and of H^1 to H^a and H^c was shown by NOE experiments.

In the cyclohexane-annelated compound **2d**, the ^{1}H NMR spectrum was best analyzed assuming that each cyclohexane ring adopted the chair form as shown in Scheme 5. Irradiation of H^4 at the lowest field of the aromatic region (δ 8.75) enhanced the lowest-field signal of the aliphatic region (δ 3.16), which was reasonably assigned to H^b. The signal appeared as a triplet ($J = 13.5$ Hz) of doublets ($J = 5.3$ Hz), suggesting that H^b is in an axial position. Meanwhile, irradiation of H^1 at δ 8.14 enhanced the signal at δ 2.26 assignable to H^c.

Table 2. ^{1}H Chemical Shifts (δ) of Trispiro[truxenetris(cycloalkane)]s **2**, Spiro[cycloalkanefluorene]s **5**, and Related Compounds in CDCl$_3$[a]

Compd	**2a**	**2b**	**2c**	**2d**	**4**	**5a**	**5b**	**5c**	**5d**	**6**
H^1	7.05	8.10	7.56	8.14	7.55	7.05	7.77	7.43	7.66[b]	7.42
H^2	7.34	7.50	7.35	7.33	7.39	7.29	7.36	7.30	7.30	7.33
H^3	7.35	7.49	7.41	7.45	7.42	7.35	7.33	7.32	7.35	7.33
H^4	8.09	8.48	7.88	8.75	8.31	7.83	7.67	7.70	7.74[c]	7.73
H^a	1.70	2.44	1.87	1.42	1.89	1.72	2.64	2.11	1.92	1.48
H^b	2.99	3.66	3.10	3.16		1.72	2.64	2.11	1.92	
H^c		2.91	2.52	2.26			2.40	2.11	1.75	
H^d		2.68	2.52	2.02			2.40	2.11	1.75	
H^e				2.10					1.81	
H^f				2.18					1.81	

a) Obtained at 22–24 °C unless otherwise stated. b) Appeared at δ 7.49 and 8.00 at -70 °C. c) Appeared at δ 7.81 and 7.86 at -70 °C.

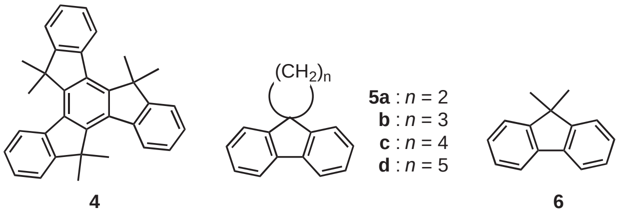
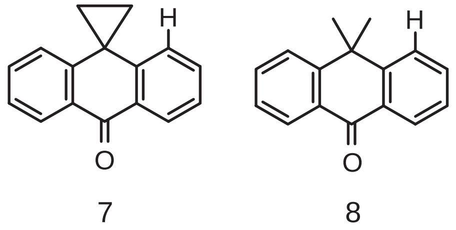
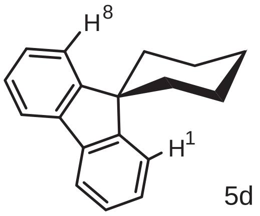


Chart 2.



Scheme 7.



Scheme 6.

The other chair form, which would be formed by ring inversion of the chair shown in Scheme 5, seemed far less stable judging from the model consideration and also from simple molecular mechanics calculations.

In Table 2 the data for 5,5,10,10,15,15-hexamethyltruxene (**4**) are also included as well as those of the corresponding spiro[cycloalkane-1,9′-fluorene]s **5a**–**5d** and of 9,9-dimethylfluorene (**6**) as the reference compounds (Chart 2). Jason and Kurzweil have reported detailed ^{1}H NMR analysis of **5a**–**5c**.[6] We re-examined the analysis and our data are compiled in Table 2; chemical shift assignments of **5b** are different from those by Jason and Kurzweil, which lacked the NOE confirmation.

The ^{1}H NMR spectrum of spiro[cyclohexane-1,9′-fluorene] (**5d**) was newly analyzed. At room temperature, inversion of the cyclohexane ring was very fast on the NMR timescale, and a fast-exchange limit spectrum was obtained. Upon lowering the temperature, the signals broadened and decoalesced, reflecting the slowing of the inversion. At -70 °C, the lowest temperature examined, the spectrum was not yet fully sharpened, but two signals assignable to H^1 and H^8 were detected at δ 7.49 and 8.00. The lower-field signal at δ 8.00 is assigned to H^1 judging from the steric congestion (Scheme 6), and this serves as the reference for **2d**.

The H^1 signal of the cyclopropane derivative **2a** appears at a higher field by 0.50 ppm than that of **4**. A similar tendency was observed in the fluorene series, **5a** vs **6**, but to a smaller extent (0.36 ppm). These phenomena are reasonably ascribed to the ring current effect of cyclopropane: H^1 in **2a** and **5a** are located in the shielding region of the flanking cyclopropane ring.[9] A similar example has been observed in an anthrone series (Scheme 7): The indicated proton in **7** appeared at a higher field by 0.51 ppm than that in **8**.[10]

The H^4 signals in the truxene series **2** resonate at the lowest field of the aromatic region and this will mainly be ascribed to the steric compression effect of the nearby cycloalkane moiety. The H^4 signals of **2b** and **2d** appear at a lower field (δ 8.48 and 8.75, respectively) than that of the reference compound **4** (δ 8.31), while those of **2a** and **2c** appear at a higher field (δ 8.09 and 7.88, respectively). The lower-field shifts in **2b** and **2d** are ascribed to the even greater steric compression in these compounds than in **4**, while the higher-field shift in **2a** is due to the ring current effect of the cyclopropane moiety. We have no definite explanation for the high field shift of H^4 in the cyclopentane compound **2c**.

Lower-field shifts due to the steric compression effect are also observed for the H^b signals in **2a**–**2d**, which are more than 1.2 ppm lower than H^a bonded to the same carbon atom.

^{13}C NMR Spectra. The ^{13}C NMR spectra of these compounds were also fully analyzed and unambiguously assigned (Table 3). C–H COSY experiments allowed assignments other than those of the quaternary carbons, which were obtained from ^{1}H-coupled and selectively ^{1}H-decoupled spectra. In spiro[cyclopropane-1,9′-fluorene] (**5a**), one quaternary carbon signal at δ 139.8 appeared as roughly a triplet ($J \approx 6$ Hz) of

Table 3. ^{13}C Chemical Shifts (δ) of Trispiro[truxenetris(cycloalkane)]s **2**, Spiro[cycloalkanefluorene]s **5**, and Related Compounds in $CDCl_3$[a)]

Compd	**2a**	**2b**	**2c**	**2d**	**4**	**5a**	**5b**	**5c**	**5d**	**6**
C^1	**117.9**	121.7	122.2	124.2	122.4	**118.6**	122.7	122.8	124.4	122.8
C^2	126.5	127.6	126.8	125.6	126.7	125.9	127.0	126.4	126.8	127.0
C^3	125.9	126.5	125.8	125.4	126.2	126.8	127.5	127.4	126.8	127.4
C^4	123.1	123.5	124.5	127.6	125.6	119.9	119.5	119.5	119.7	120.1
C^{4a}	137.2	137.4	136.7	137.2	136.7	139.8	139.3	139.5	139.6	139.2
C^{15a}	**150.5**	156.7	158.6	156.7	157.5	**148.1**	152.2	154.2	153.1	153.7
C^{4b}	135.8	137.6	135.8	135.0	135.7	—	—	—	—	—
C^{14c}	142.6	144.5	146.7	150.2	148.2	—	—	—	—	—
C^{15}	31.2	51.7	59.3	49.5	46.8	29.4	51.8	57.6	50.2	46.8
C^{α}	16.8	30.2	34.6	27.5	24.0	18.3	33.2	39.7	35.6	27.3
C^{β}	—	16.8	25.8	21.6	—	—	17.0	26.9	22.6	—
C^{γ}	—	—	—	22.9	—	—	—	—	25.6	—

a) The numberings of the carbon atoms are shown in Scheme 3. Chemical shifts shown in bold letters are remarkable and discussed in the text.

doublets ($J \approx 3$ Hz), while the other one at δ 148.1 appeared as a complex multiplet. When the cyclopropane protons were selectively irradiated, the latter signal became a sharp triplet ($J \approx 6$ Hz). It is well documented that $^3J_{CH}$ is generally larger than $^2J_{CH}$ and that, for the aromatic carbons, $^3J_{CH}$ with a *meta* proton is 6–7 Hz, while $^2J_{CH}$ with an *ortho* proton is far smaller (less than 1 Hz). Judging from these facts, the signal at δ 139.8 in **5a** is reasonably assigned to C^{4a}, while that at δ 148.1 is assigned to C^{15a}, as given in Table 3 (The numbering follows that in Scheme 2): C^{15a} couples with H^2 and H^4 (both *meta*; $J \approx 6$ Hz) and also with the cyclopropane protons (three-bond), while C^{4a} couples with H^1 and H^3 (both *meta*; $J \approx 6$ Hz), and also with H^5 (not *meta* but three-bond; $J \approx 3$ Hz). The carbon chemical shifts for the other compounds in the fluorene series **5** were similarly assigned and are compiled in Table 3.

The ^{13}C NMR spectra of the truxene series **2** were similarly analyzed. Among the four quaternary carbon signals in **2a**, those at δ 135.8 and 137.2 appeared as a doublet ($J \approx 2$ Hz) and triplet ($J \approx 6$ Hz), respectively, in the ^{1}H-coupled spectrum, while those at δ 142.6 and 150.5 appeared as complex multiplets. When the H^4 signal at δ 8.09 was irradiated, the signal at δ 135.8 became a sharp singlet and that at δ 150.5 was considerably narrowed, while those at δ 137.2 and 142.6 did not change at all. Therefore, all the carbons in **2a** were unambiguously assigned as given in Table 3. The chemical shifts of the other truxene compounds were similarly assigned and are compiled in Table 3.

In the fluorene series **5**, C^1 and C^{15a} (C^{8a} by the fluorene nomenclature) in **5a** are remarkable: They appear at a higher field by ca. 4 ppm than the corresponding carbons in the other members of the series, while the carbons other than C^1 and C^{15a} have similar chemical shifts as the respective carbons in the series. In the truxene series **2**, C^1 and C^{15a} in **2a** are unique.

UV–Vis Spectra. The electronic spectra of the truxenes **2a**–**2d** and the fluorenes **5a**–**5d** in CH_2Cl_2 are shown in Fig. 2. In the truxene series, the longest wavelength bands showed bathochromic shifts by 6 to 20 nm compared with that of the parent truxene **1** (**2a**: 318, **2b**: 312, **2c**: 306, **2d**: 304, **1**: 298 nm). On the other hand, the longest wavelength bands in the fluorene series showed only slight bathochromic shifts compared with those of fluorene (**5a**: 302, **5b**: 305, **5c**: 303, **5d**: 301, fluorene: 300 nm).

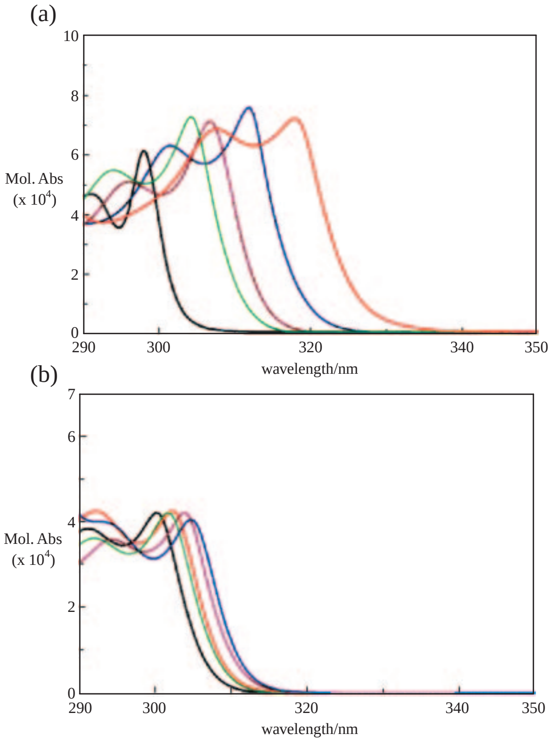
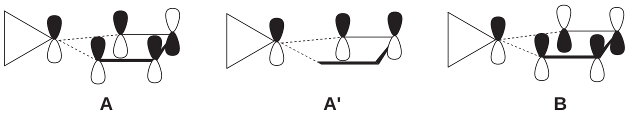


Fig. 2. UV spectra in CH_2Cl_2 at room temperature of (a) **2a** (red), **2b** (blue), **2c** (purple), **2d** (green), and **1** (black), and (b) **5a** (red), **5b** (blue), **5c** (purple), **5d** (green), and fluorene (black).

It is well known that small aliphatic rings such as cyclopropane behave as an electron donor substituent for various π-conjugated systems. It is explained that the 1e′ orbital (HOMO) of cyclopropane lies at a high energy level compared to most carbon–carbon σ orbitals and the relatively large p character of the σ orbital at the ring juncture of the cyclopropyl group can make more effective σ–π interactions with neighboring π orbitals.[8] As the ring size of cycloalkane becomes larger, the extent of bathochromic shifts becomes small-



Scheme 8.

er, reflecting the decrease in the interactions mentioned above. Although the two series **2a**–**2d** and **5a**–**5d** have similar structures around the cycloalkane ring, the extent of the bathochromic shifts of both series were clearly different.

In order to probe into this, CNDO/S calculations were performed for **2a**, **1**, **5a**, and fluorene.[11] The two degenerated HOMOs of **2a** were found to lie at a higher energy level than those of **1**, suggesting orbital mixing of the cyclopropane and truxene moieties, while the HOMO level of **5a** is almost the same as that of fluorene, indicating that the σ–π interactions between the cyclopropane and fluorene moieties canceled out each other. It is inferred that this comes from the difference in the phase relation of the HOMO orbital between **2a** and **5a**. In **2a**, the phase relations are schematically shown as **A** and **A′** in Scheme 8, while that in **5a** is shown as **B**. Therefore, the bathochromic shifts in the truxene series **2a**–**2d** are ascribed to the preferable σ–π interaction.

In conclusion, the cycloalkane-annelated truxenes **2a**–**2d** have been shown to behave rather similarly to the corresponding fluorenes **5a**–**5d**. Although a comparison of ^{1}H and ^{13}C NMR chemical shifts between **2a**–**2d** and **5a**–**5d** could not explicitly show the spiro-annelation effects, the σ–π orbital interactions between the cycloalkane part and the truxene moiety of **2a**–**2d** were more clearly reflected on an electronic spectra than those of **5a**–**5d**, which were attributed to a difference in the orbital phase relations of both series.

We are now extending the studies to a system where three-unsaturated rings, such as fluorene and 4,5-diazafluorene, are spiro-annelated to the truxene skeleton.

Experimental

General. Melting points are not corrected. Mass spectra were obtained on a Hitachi M-2500 spectrometer in the EI mode. IR spectra were obtained on a Jasco FT/IR-610 spectrometer. UV–vis spectra were obtained on a Jasco V-560 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ARX-300 spectrometer operating at 300.1 MHz for ^{1}H and 75.4 MHz for ^{13}C. Chemical shifts are referenced with internal tetramethylsilane ($\delta_H = 0.00$) and $CDCl_3$ ($\delta_C = 77.00$). In variable-temperature experiments, temperatures were calibrated using a methanol sample or an ethylene glycol sample and are reliable to ±1 °C. Preparative gel permeation chromatography (GPC) was performed on an LC-908 liquid chromatograph (Japan Analytical Industry Co., Ltd.) using a series of JAIGEL 1H and 2H columns with chloroform as the eluent.

The reference compounds were synthesized according to the literature: **4**,[12] **5a**–**5c**,[6] **5d**,[13] and **6**.[14]

General Procedure for the Syntheses of Trispiro[truxene-5,1′:10,1″:15,1‴-tris(cycloalkane)]s 2. To a solution of truxene (**1**) (1.00 g, 2.93 mmol) in THF (50 mL) was added a solution of BuLi in hexane (5.66 mL, 1.58 mol L^{-1}, 9.06 mmol) at 0 °C and the mixture was stirred at 0 °C for 0.5 h, then warmed slowly to room temperature. To the reaction mixture was added 1,ω-dibromoalkane (10.2 mmol) at room temperature, and the mixture was stirred for 0.5 h, treated with water, then extracted with AcOEt. The extracts were dried over $MgSO_4$ and evaporated. Column chromatography (silica gel, hexane) gave the 5,10,15-tris(ω-bromoalkyl)truxene **3** as yellow solids. ^{1}H NMR of **3** showed that it consisted of two stereoisomers, *syn* and *anti*, in a ratio of ca. 1:3. The product obtained was used without further purification in the next reaction.

To a solution of the tris(ω-bromoalkyl)truxene **3** in THF (50 mL) at 0 °C was added potassium hydride (5 equiv). The reaction mixture was stirred at room temperature for 6 h, treated with water, and then extracted with benzene. The extracts were dried over $MgSO_4$ and evaporated. Column chromatography (silica gel, hexane) gave the corresponding trispiro[truxene-5,1′:10,1″:15,1‴-tris(cycloalkane)] **2**.

Trispiro[truxene-5,1′:10,1″:15,1‴-tris(cyclopropane)] (2a): **2a** was obtained in 71% yield as pale yellow needles (from CH_2Cl_2), mp 271–272 °C (dec). Found: C, 94.37; H, 5.97%. Calcd for $C_{33}H_{24}$: C, 94.25; H, 5.75%. ^{1}H NMR ($CDCl_3$) δ 1.70 (6H, m), 2.99 (6H, m), 7.05 (3H, m), 7.34 (3H, m), 7.35 (3H, m), 8.09 (3H, m). ^{13}C NMR ($CDCl_3$) δ 16.8 (6C, s), 31.2 (3C, q), 117.9 (3C, t), 123.1 (3C, t), 125.9 (3C, t), 126.5 (3C, t), 135.8 (3C, q), 137.2 (3C, q), 142.6 (3C, q), 150.5 (3C, q). MS m/z 420 (M$^+$), 392, 362. IR (KBr) 3043, 3010, 2923, 1473, 1437, 1369, 736 cm^{-1}. UV (CH_2Cl_2) $\lambda_{\max}$ ($\log \varepsilon$) 318 (4.89), 307 (4.86), 284 (4.76) nm.

Trispiro[truxene-5,1′:10,1″:15,1‴-tris(cyclobutane)] (2b): **2b** was obtained in 80% yield as yellow prisms (from AcOEt), mp 290–291 °C (dec). Found: C, 93.67; H, 6.54%. Calcd for $C_{36}H_{30}$: C, 93.46; H, 6.54%. ^{1}H NMR ($CDCl_3$) δ 2.44 (6H, m), 2.68 (3H, m), 2.91 (3H, m), 3.66 (6H, m), 7.49 (3H, m), 7.50 (3H, m), 8.10 (3H, m), 8.48 (3H, m). ^{13}C NMR ($CDCl_3$) δ 16.8 (3C, s), 30.2 (6C, s), 51.7 (3C, q), 121.7 (3C, t), 123.5 (3C, t), 126.5 (3C, t), 127.6 (3C, t), 137.4 (3C, q), 137.6 (3C, q), 144.5 (3C, q), 156.7 (3C, q). MS m/z 462 (M$^+$), 434, 406, 378. IR (KBr) 3043, 3021, 2940, 1473, 1438, 1367, 736 cm^{-1}. UV (CH_2Cl_2) $\lambda_{\max}$ ($\log \varepsilon$) 312 (4.89), 301 (4.81), 281 (4.76) nm.

Trispiro[truxene-5,1′:10,1″:15,1‴-tris(cyclopentane)] (2c): **2c** was obtained in 71% yield as colorless solids (from hexane), mp 283–284 °C (dec). Found: C, 92.93; H, 7.28%. Calcd for $C_{39}H_{36}$: C, 92.81; H, 7.19%. ^{1}H NMR ($CDCl_3$) δ 1.87 (6H, m), 2.52 (12H, m), 3.10 (6H, m), 7.35 (3H, td, $J = 7.3$, 1.0 Hz), 7.41 (3H, td, $J = 7.5$, 1.5 Hz), 7.56 (3H, dd, $J = 7.3$, 1.5 Hz), 7.88 (3H, d, $J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$) δ 25.8 (6C, s), 34.6 (6C, s), 59.3 (3C, q), 122.2 (3C, t), 124.5 (3C, t), 125.8 (3C, t), 126.8 (3C, t), 135.8 (3C, q), 136.7 (3C, q), 146.7 (3C, q), 158.6 (3C, q). MS m/z 504 (M$^+$), 446, 388. IR (KBr) 3035, 3033, 2962, 2925, 1467, 1373, 1317, 742 cm^{-1}. UV (CH_2Cl_2) $\lambda_{\max}$ ($\log \varepsilon$) 306 (4.88), 296 (4.77), 278 (4.78) nm.

Trispiro[truxene-5,1′:10,1″:15,1‴-tris(cyclohexane)] (2d): **2d** was obtained in 27% yield as colorless solids (from hexane), mp 283–284 °C (dec). Found: C, 91.84; H, 7.78%. Calcd for $C_{42}H_{42}$: C, 92.26; H, 7.74%. ^{1}H NMR ($CDCl_3$) δ 1.42 (6H, dd, $J = 13.5$, 4.2 Hz), 2.02 (6H, m), 2.10 (3H, m), 2.18 (3H, m), 2.26 (6H, m), 3.16 (6H, td, $J = 13.5$, 5.3 Hz), 7.33 (3H, t, $J = 7.3$ Hz), 7.45 (3H, td, $J = 7.6$, 1.0 Hz), 8.14 (3H, dd, $J = 7.7$, 0.8 Hz), 8.75 (3H, d, $J = 7.6$ Hz). ^{13}C NMR ($CDCl_3$) δ 21.6 (6C, s), 22.9 (3C, s), 27.5 (6C, s), 49.5 (3C, q), 124.2 (3C, t), 125.4 (3C, t), 125.6 (3C, t), 127.6 (3C, t), 135.0 (3C, q), 137.2 (3C, q), 150.2 (3C, q), 156.7 (3C, q). MS m/z 546 (M$^+$), 474, 402. IR (KBr) 3060, 3035, 2929, 1454, 1373, 1367, 742 cm^{-1}. UV (CH_2Cl_2) $\lambda_{\max}$ ($\log \varepsilon$) 304 (4.88), 294 (4.76), 277 (4.78) nm.

X-ray Crystallographic Analyses of 2a. Crystals of compound **2a** were grown from dichloromethane–hexane. The crystal

Table 4. Crystal Data of **2a** and Parameters for Data Collection, Structure Determination, and Refinement

Empirical formula	$C_{33}H_{24}$
Formula weight	420.52
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	26.483(6)
b/Å	7.780(1)
c/Å	20.607(3)
V/Å^3	4245(1)
Z	8
D_{calcd}/g cm^{-3}	1.316
$F(000)$	1776
μ(Mo Kα)/cm^{-1}	0.074
Temp/K	102(1)
$2\theta_{\mathrm{max}}$/°	55
No. of reflections measured	
Total	9635
Unique ($I > 2\sigma(I)$)	8818
No. of refinement variables	595
Final $R1$;[a] $wR2$[a]	0.069; 0.170
GOF	1.084

a) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ on F^2, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0914P)^2 + 2.7533P]$ where $P = (F_o^2 + 2F_c^2)/3$.

data and the parameters for data collection, structure determination, and refinement are summarized in Table 4. X-ray data were collected using a Rigaku-AFC8R diffractometer equipped with an MSC/Mercury CCD area detector at 102 ± 1 K. Data collection control and reduction were performed by MSC/CrystalClear version 1.35. Absorption corrections were applied by a multi-scan technique with the T range of 0.8624 to 1.00. The structure was solved by a direct method and refined on F squared by using the SHELXS-97 and SHELXL-97 programs.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic parameters.

Crystallographic data of **2a** has been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-297312. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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