Synthesis and Diatropicity of *trans*-2′,5′,10b,10c-Tetramethylfurano[3,4-*e*]-10b,10c-dihydropyrene. A Valence Isomerization To Form a Novel Isoannulenofuran at the Expense of Two Benzene and One Furan Rings

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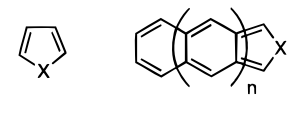
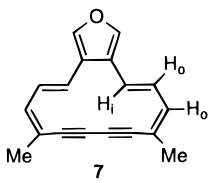
The 1,4-dicarbonyl compound **22** was prepared by an oxidative coupling of the benzyl methyl ketone **19**. Dehydration of **22** gave the 3,4-diarylfuran **16** which upon functional group transformations and a subsequent intramolecular cyclization afforded only the *anti* isomer of the furanothiacyclophane **27**. Ring contraction following a Wittig rearrangement−Hofmann elimination sequence led to the isolation of *anti* furanocyclophanene **15b**. Valence isomerization of **15b** to the isoannulenofuran **14b** could be achieved either photochemically or thermally with **15b** as the thermodynamically more stable isomer. Compound **14b** was found to exhibit only a very small ring current. The diatropicity of **14b** is clearly affected by a weak participation of the oxygen in π-electron delocalization and a steric effect of its external methyl groups resulting in a deviation from planarity of its molecular periphery. The thermal conversion of **15b** to **14b** was determined to have a high activation energy of 114 kJ mol^{-1}. This thermal process, in addition to involving the disruption of π-electron delocalization in two benzene and one furan rings, is another example of an unsual concerted, symmetry-forbidden reaction.

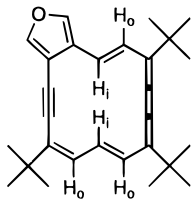
The aromaticity of the heterocycles pyrrole (**1**), furan (**2**), and thiophene (**3**) has been well studied in terms of both chemical and physical properties.[1,2] The general conclusion has always been that furan (**2**) is the least aromatic. The fusion of these heterocycles at the 3,4-positions to unsaturated carbocycles, *i.e.*, isoannelation, has also been examined. Results from the calculations[3] of the topological resonance energy per π-electron for the series of isoannelated compounds **4**−**6** again indicate that **5** is the least aromatic. The participation of oxygen in





the aromaticity of the resulting isoannelated macroring thus seems to be the least effective of the selected heteroatoms. Deshielded signals (δ 7.8−8.4)[4] experimentally observed for the furanoid protons in the ^{1}H NMR spectrum of **5** (n = 0), however, suggests the presence of a strong ring current and somewhat contradicts the data obtained from theoretical calculations.

Among the few reported isoannulenofurans[5] (oxa[17]-annulenes), compound **7** ($|\delta H_i - \delta H_o| \approx 0$)[6] is essentially nondiatropic, while there is a significant decrease in diatropicity in compound **8** ($|\delta H_i - \delta H_o| \approx 3$)[7] relative to that of the benzo[14]annulene **9** ($|\delta H_i - \delta H_o| \approx 8$).[8]



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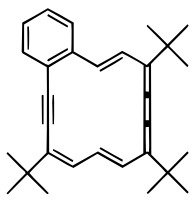
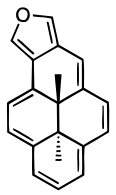


9

Compound **8** is not very stable, and its aromatic protons are likely to be affected by local anisotropic effects.[9] The [*a*]-ring furano-annelated dihydropyrene **10** (δCH_3 = 0.13, 0.15)[10] has also qualitatively been found to exhibit only about 16% of the ring current of the parent compound **11** ($\delta CH_3 = -4.25$).[11] The cyclophanediene **12** was



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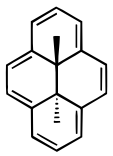

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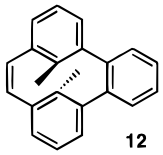

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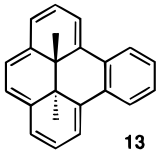

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(1) *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon Press: New York, 1984; Vol. 4.

(2) Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulene, Benzo-, Hetero-, Homo-Derivatives and Their Valence Isomers*; CRC Press: Boca Raton, FL, 1987; Vol. 3.

(3) Jurić, A.; Sabljić, A.; Trinajstić, N. *J. Heterocycl. Chem.* **1984**, *21*, 273.

(4) (a) Warrener, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346. (b) Wege, D. *Tetrahedron Lett.* **1971**, 2337. (c) Wiersum, U. E.; Mijs, W. J. *J. Chem. Soc., Chem. Commun.* **1972**, 347.

(5) This term is derived qualitatively from isobenzofuran.

(6) (a) Beeby, P. J.; Weavers, R. T.; Sondheimer, F. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 138. (b) Weavers, R. T.; Sondheimer, F. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 141.

(7) (a) Ebe, H.; Nakagawa, T.; Iyoda, M.; Nagakawa, M. *Tetrahedron Lett.* **1981**, *22*, 4441. (b) Iyoda, M.; Nakagawa, T.; Ebe, H.; Oda, M.; Nakagawa, M.; Yamamoto, K.; Higuchi, H.; Ojima, J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 778.

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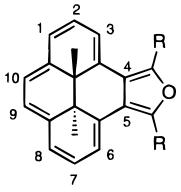
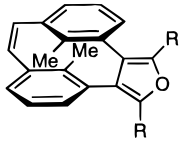
reported to undergo valence isomerization[12] readily to give the [*e*]-ring annelated benzo[14]annulene **13** ($\delta CH_3 = -1.85$)—an example of interrupting the delocalization of π-electrons in three benzene rings to form a benzannelated dihydropyrene. Many other benzannelated derivatives of **11** were found to behave similarly.[13] The high diatropicity (aromaticity) achieved in the dihydropyrene moiety is believed to be one of the main driving forces for such a conversion. Given the fact that isoannelation would only lead to a significantly less diatropic (aromatic) macroring, it would thus be doubtful whether an isoannulenofuran such as **14a** could be obtained from the valence isomerization of **15a** at the expense of two benzene and one furan rings. We wish to report the



14 a, R = H
b, R = CH_3

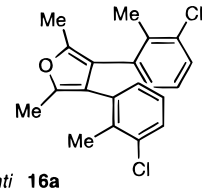


15 a, R = H
b, R = CH_3

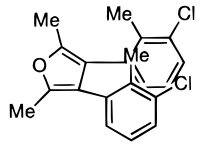
synthesis of cyclophanene **15b** and its physical and chemical properties.

Results and Discussion

(a) Synthesis. The synthesis of [*e*]-ring annelated derivatives of **11** commonly involves, as a precursor, a suitably substituted *tert*-aryl derived from an *o*-dibromo aromatic compound or an *o*-quinone.[10b,12−14] These approaches are, however, inappropriate for the synthesis of a 3,4-diarylfuran. In order to minimize any complication from addition and/or substitution reactions at the 2,5-positions of a furan ring, we have selected the 3,4-diarylfuran **16** as a synthetic precursor for **15b**.

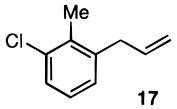


anti **16a**



syn **16a**

Treatment of the mono-Grignard[15] prepared from 2,6-dichlorotoluene with 3−bromopropene gave compound **17**. Conversion of **17** to the alcohol **18** was achieved by an oxymercuration/demercuration[16] sequence in quantitative yield. The oxidation of **18** with Jones' reagent[17] in acetone afforded the desired ketone **19**. A side product, the aldehyde **20**, was obtained from this reaction, and its yield increased with reaction time. This, we believe, was due to further oxidation of **19** at the benzylic position followed by oxidative cleavage. Alternatively, the ketone **19** could be synthesized by the treatment of the mono-Grignard prepared from 2,6-dichlorotoluene with 3-bromo-2-methoxy-1-propene[18] to give the intermediate **21** followed by an acid hydrolysis of the latter.



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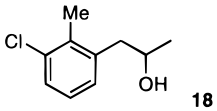

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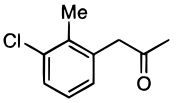

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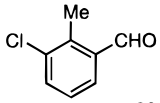

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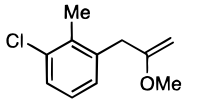
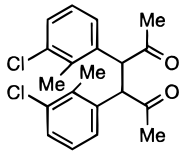


21

The 1,4-dicarbonyl compound **22** was then prepared via an oxidative coupling of **19** with activated manganese dioxide in acetic acid.[19] This reaction in fact afforded a mixture of the diketone **22** and the diarylfuran **16** in 18% and 9% yield, respectively. These two compounds could be separated readily by column chromatography. The latter was clearly formed by the acid-catalyzed dehydration of the former. In fact, dehydration[20] of **22** with phosphorus pentoxide in a mixture of THF and ethanol gave the desired 3,4-diarylfuran **16** in good yield. Sterically, the *anti* conformation **22a** is expected to be the most stable. In the ^1H NMR spectrum of **22**, however, the aryl methyl protons appeared at δ 1.84—significantly shielded compared to the methyl protons of toluene (δ 2.35).[21] This shielding is consistent with an *anti*-stepped conformation with a hydrogen bond between the two acetyl groups as shown in **22b**. For the diarylfuran **16**, its ^1H NMR spectrum showed two singlets at δ 2.16 and 2.15 (1:1) which correspond to the methyl groups on the benzene rings. Their resolution indicates the presence of *anti* and *syn* conformers **16a** and **16b**, respectively, similar to that observed in other *tert*-aryl systems.[22,23] The methyl groups on the furan ring were, however, unresolved and appeared as a singlet at δ 2.09.



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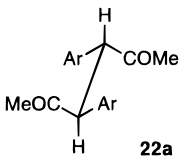
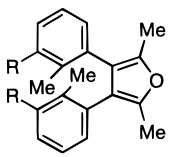
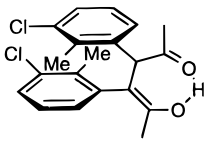


22a



23 R = CN
24 R = CHO
25 R = CH_2OH
26 R = CH_2Br



22b

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(16) Brown, H. C.; Geoghegan, P. J., Jr. *J. Org. Chem.* **1970**, *35*, 1844.
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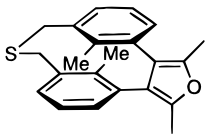
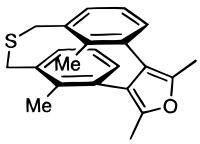
Conversion of **16** to **26** was achieved with minor modifications via a similar sequence of reactions reported for the syntheses of the corresponding 1,2-diarylbenzenes[10b,12,22] and 9,10-diarylphenanthrenes.[14] The optimized overall yield of dibromide **26** was about 58%. The existence of *anti* and *syn* conformers in this series of compounds is evident by the resolution of the corresponding pairs of methyl groups on the furan and/or benzene ring. The chemical shift difference of each pair is, however, very small and considered unreliable to serve as a probe for dynamic ^{1}H NMR studies for the estimation of the conformational energy barrier.[24]

An intramolecular coupling of the dibromide **26** with sodium sulfide under high dilution conditions[25] afforded the thiacyclophane **27**. Only its *anti* isomer **27a**, mp 208−211 °C, was isolated. There was no detectable quantity of the corresponding *syn* isomer **27b**. The *anti* stereochemistry of **27a** was confirmed by its significantly shielded internal methyl protons at δ 0.87 similar to that reported for *anti* **28** (δ 0.94).[12] The bridging methylene protons of **27a** appeared as an AB quartet at δ 3.79 and 3.67.

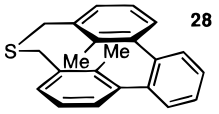


27a



27b

A general synthetic approach to the parent dimethyldihydropyrene **11**[11] and its derivatives involving ring contraction reactions of thiacyclophanenes or dithiacyclophanes has been well documented.[10b,13,26] Thus, a Wittig rearrangement[27] of **27a** with *n*-butyllithium followed by methyl iodide quench gave only the *anti* metacyclophane **29**. Its internal methyl protons are unresolved and appear as a sharp singlet at δ 0.54—shifted further upfield due to a closer stacking of the opposite benzene rings when one of the bridges is shortened going from **27a** to **29**. The above observation suggests that the SCH_3 group in **29** occupies a pseudoaxial position projecting away from the adjacent methyl group, thus resulting in no significant deshielding effect by the sulfur atom. Remethylation of **29** with dimethoxycarbonium fluoroborate[28] gave the intermediate sulfonium salt **30**, which upon treatment with potassium *tert*-butoxide in THF at room temperature led to the isolation of colorless crystals of the *anti* cyclophanene **15b** in 96% yield. Due to a gradual thermal conversion to **14b** (see later discussion) the melting point of **15b** could only be estimated to be 135−137 °C. Retention of the *anti* stereochemistry in **15b** is supported by its shielded internal methyl protons at δ 1.38 comparable to that observed for *anti* **31** (δ 1.41).[12]



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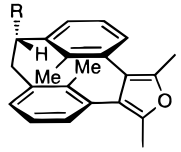
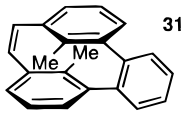
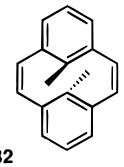




31

29 R = SMe
30 R = $S^+Me_2BF_4^-$

(b) Valence Isomerization and Diatropicity. The reversible photochemical valence isomerization[29] between dimethyldihydropyrene **11** and cyclophanediene **32** is a unique and interesting physical property of **11**. This phenomenon was also observed in most derivatives of **11**.[13,29] The conversion of **11** to **32** could be achieved by irradiation with visible light, and the reversed process was favored by irradiation with UV light.



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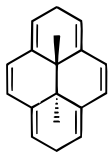

33

A pale yellowish solution of **15b** in thoroughly degassed benzene, when irradiated with UV light at 254 nm for 20 min, resulted in a dark purple solution containing a mixture of **15b** and its valence isomer, *trans*-**14b**. The presence of the latter was evident by the appearance of two new singlets at δ 0.63 and 2.38 in a 1:1 ratio in the ^{1}H NMR spectrum. A similar spectrum could also be obtained thermally by warming a solution of **15b**. It is clear that the oxa[17]annulene **14b** sustains a weak diamagnetic ring current resulting in only a small shielding of the internal methyl protons compared with those in a nonaromatic reference **33** (δCH_3 = 0.97).[30] Complete conversion of **15b** to **14b**, however, was not possible either thermally or photochemically, and prolonged reaction times seemed to result in decomposition of the product(s). The formation of **14b** was, however, confirmed by its reversed isomerization to **15b** when the solution was irradiated with visible light.

Only a single maximum was observed at 230 nm in the UV/vis spectrum of **15b**. The spectrum for a mixture of **14b** and **15b** (Figure 1) clearly shows new bands of **14b** in the range of 250−600 nm similar to those of the parent **11**[31] and benzannelated derivative **13**.[12] The maxima of **14b** in the range of 280−380 nm are, however, significantly blue shifted.

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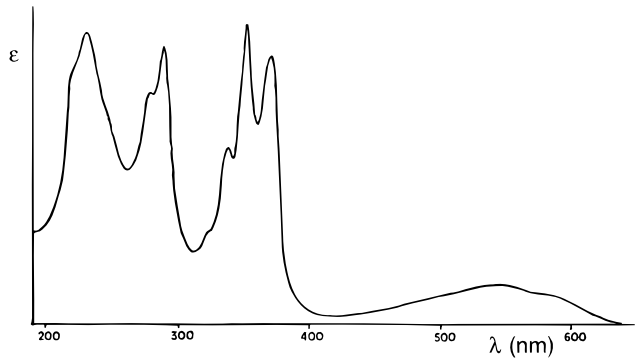
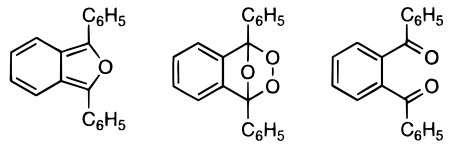


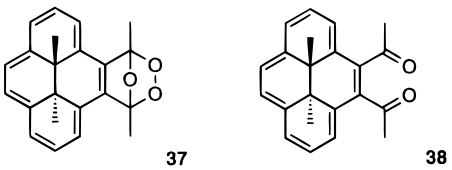
Figure 1. UV/vis absorption spectrum of a mixture of **14b** and **15b** taken in cyclohexane.

An interesting observation was that when no precaution was taken to exclude air thoroughly decomposition of **14b** was more apparent during the photochemical experiments. Irradiation of 1,3-diphenylisobenzofuran (**34**) in the presence of oxygen was reported[32] to give an ozonide **35** followed by formation of the diketone **36**.



34 **35** **36**

When a solution of **15b** was irradiated with light at 254 nm for a longer reaction time (2.5 h) with no precaution to exclude air, a dark violet solution was obtained with significant decomposition as evident by formation of insoluble solids. The ^{1}H NMR spectrum of the product mixture showed a strongly shielded singlet at δ −3.97 and a deshielded singlet at δ 2.77 in a 1:1 ratio. The above observation suggests the formation of **37** followed by that of **38**. The internal methyl protons (δ −3.97) of **38** are expected to be shielded similarly as those (δ −4.25) in the parent **11**; the external methyl protons of **38** observed at δ 2.77 are typical of conjugated acetyl groups. The presence of **38** was further supported by a peak, albeit weak, at m/z 316 in the mass spectrum of the product mixture. All attempts to isolate **38**, however, failed. Chromatography of the product mixture, directly or after irradiation with visible light, always recovered only the cyclophanene **15b** in varied yields. Apparently the dihydropyrene **38**, due to unknown reasons, was too unstable to be isolated.



37 **38**

The dihydropyrene **11** and its derivatives are usually the thermodynamically more stable isomers relative to their corresponding cyclophanedienes. The photochemical or thermal conversion of **15b** to **14b** could, however, be driven only up to an optimum buildup concentration of about 50% of **14b**. This process is thus significantly less favorable than that of **32** → **11**[29] or **12** → **13**.[12] An obvious explanation is a significantly lower diatropicity

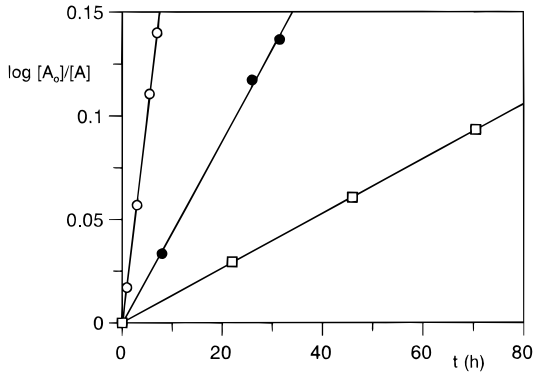
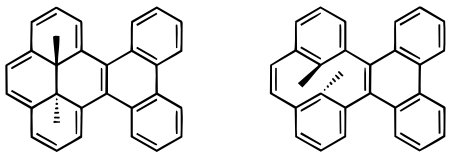


Figure 2. Plot of log [A_o]/[A] against time for valence isomerization of **15b** to **14b**: □, 39 °C; ●, 49 °C; ○, 59 °C.

(aromaticity) of the isoannelated compound **14b** (internal methyl protons at δ 0.63). Assuming that proton shielding is proportional to ring current,[33] **14b** exhibits only <7% of the ring current of **11** ($\delta CH_3 = -4.25$)—a value about 10% lower than that of the [*a*]-ring annelated system **10** (δCH_3 = 0.13, 0.15). This we believe is associated with the steric interactions derived from the external methyl groups in **14b** resulting in a deviation from planarity of its molecular periphery. "Bay-area" steric interactions in **39** were also reported to be responsible for a preference to cyclophanediene **40** in their valence isomerization processes.[14]

The activation energy for the conversion of **32** → **11** was determined by UV spectroscopy[29] due to fast reaction rates. ^{1}H NMR spectroscopy is, however, a more suitable method to measure the activation energy for the relatively slower conversion of **12** → **13**[12] or **40** → **39**.[14] The



39 **40**

slow thermal conversion of **15b** → **14b** was thus examined by ^{1}H NMR spectroscopy. From a plot of log[A_o]/[A] against time (Figure 2), where [A_o] is the initial concentration of **15b** and [A] the concentration of **15b** at time t, the rate constants, k, at 39, 49, and 59 °C, respectively, were determined to be 8.32×10^{-7}, 2.81×10^{-6}, and 1.30×10^{-5} s^{-1}. The rate constants for conversions of **32** → **11**[29] and **12** → **13**[12] were found to be 1.67×10^{-5} and 0.73×10^{-5} s^{-1} at 30 and 32 °C, respectively, thus supporting qualitatively a significantly slower conversion rate for **15b** → **14b**. From a plot of −log k against $1/T$ (Figure 3), the energy of activation, E_{act}, for **15b** → **14b** was estimated to be 114 kJ mol^{-1} compared to values of 97 and 105 kJ mol^{-1}, respectively, for **32** → **11**[29] and **12** → **13**.[12]

Conclusion

Isoannelation and a poor participation of oxygen in sustaining a ring current in an oxa[17]annulene clearly results in a drastic decrease in diatropicity going from **11** (100%) to **13** (54%) to **14b** (<7%). This order is also reflected in an increase in the energy of activation for

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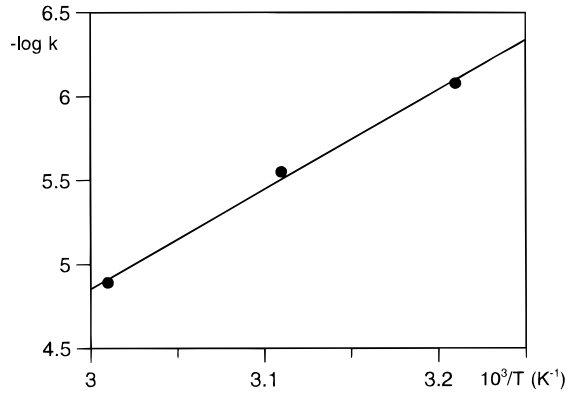

Figure 3. Plot of −log *k* against reciprocal absolute temperature for the valence isomerization of **15b** to **14b**.

the valence isomerization of **32** → **11** (97 kJ mol^{-1}), **12** → **13** (105 kJ mol^{-1}), and **15b** → **14b** (114 kJ mol^{-1}). An interesting result is obviously the fact that cyclophanene **15b** is the thermodynamically more stable isomer in contrast to the parent **11** and most of its derivatives. Despite all the unfavorable thermodynamic factors, it was rather surprising to observe thermally the formation of isoannulenofuran **14b** at the expense of interrupting the π-electron delocalization in two benzene and one furan rings in **15b**. This is especially novel since the general thermal valence isomerization of **32** → **11** represents one of those unusual concerted, symmetry-forbidden reactions.[29] Another favorable driving force for such a conversion is believed to derive from the exceptional symmetrical and rigid molecular structure of the 10b,10c-dihydropyrene system.

Experimental Section

All melting points were determined with a Sybron-Thermolyne MP-12615 melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined in $CDCl_3$ on a JEOL FX90Q (90 MHz) or a Bruker ACF300 (300 MHz) spectrometer. All proton chemical shifts are reported in ppm downfield from TMS, which was used as an internal standard. IR spectra were recorded on a Perkin-Elmer 1310 spectrometer. UV/vis spectra were determined in cyclohexane on a Shimadzu UV240 Graphicord spectrometer. EIMS was determined on a VG Micromass 7035 mass spectrometer at 70 eV. Relative intensities are given in parentheses. Only the molecular ion containing ^{35}Cl and/or ^{79}Br is given for any compound containing chlorine and/or bromine; the correct isotope pattern was obtained in each case. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore. All evaporations were carried out under reduced pressure on a rotary evaporator at about 40 °C, and all organic layers were washed with water, unless otherwise stated, and dried with anhydrous magnesium sulfate.

3-(3-Chloro-2-methylphenyl)propene (17). To a solution of the mono-Grignard reagent prepared[15] from 2,6-dichlorotoluene (48.3 g, 0.30 mol) in dry THF cooled in an ice bath was added 1-bromo-3-propene (36.3 g, 0.30 mol). The reaction mixture was allowed to warm to room temperature, stirred for 15 h, cooled in an ice bath, and hydrolyzed with H_2SO_4/H_2O (1:1) until all solids dissolved. The mixture was extracted with ether, washed, dried, and evaporated. The product **17** was collected as a colorless liquid at 212−214 °C upon distillation at 760 mmHg: 39.5 g (79%); ^{1}H NMR δ 7.0−7.3 (m, 3 H), 5.70−6.14 (m, 1 H), 4.82−5.23 (m, 2 H), 3.37 (d, 2 H, J = 5.9 Hz), 2.31 (s, 3 H); IR (neat) 3080, 1640, 1570, 1440, 1405, 1310, 1200, 1165, 1135, 1010, 990, 840, 780, 720, 670 cm^{-1}; MS *m*/*z* 166 (M$^+$, 40), 151 (10), 131 (100), 116 (23), 115 (20), 91 (21). Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65. Found: C, 72.00; H, 6.48.

1-(3-Chloro-2-methylphenyl)propan-2-ol (18). Compound **17** (5.00 g, 30 mmol) was added to a solution of mercuric acetate in water (30 mL) and THF (30 mL). The reaction mixture was stirred at room temperature for 30 min. Aqueous NaOH (3.0M, 30 mL) was added to the mixture followed by a solution of 0.5 M sodium borohydride in 3.0 M NaOH (30 mL). After the mercury had settled, the reaction mixture was extracted with dichloromethane, washed, dried, and evaporated to give a quantitative yield of the alcohol **18** isolated as a colorless oil: 5.51 g (100%); ^{1}H NMR δ 7.1−7.4 (m, 3 H), 3.90−4.12 (m, 1 H), 2.81 (d, 2 H, J = 6.3 Hz), 1.64 (s, 1 H), 1.38 (s, 3 H), 1.26 (d, 3 H, J = 6.3 Hz); IR (neat) 3380 (OH), 2960, 2920, 1560, 1370, 1110, 1080, 1000, 930, 910, 770, 710 cm^{-1}; MS *m*/*z* 184 (M$^+$, 17), 140 (87), 105 (100), 91 (6); M_r calcd for $C_{10}H_{13}ClO$ 184.0655, found (MS) 184.0642.

1-(3-Chloro-2-methylphenyl)propanone (19). (a) Jones' reagent[17] (4.1 mL) was added dropwise to a solution of the alcohol **18** (2.00 g, 10.8 mmol) in acetone (50 mL) cooled in an ice bath. The reaction mixture was stirred for 2 min at room temperature and diluted with water (50 mL). The mixture was then extracted with ether. The organic layer was washed with water, dried, and evaporated. The crude product was chromatographed on silica gel using dichloromethane/hexane (1:1) as eluent to give the ketone **19** isolated as a pale yellow liquid: 1.20 g (60%); ^{1}H NMR δ 7.0−7.3 (m, 3 H), 3.75 (s, 2 H), 2.26 (s, 3 H), 2.15 (s, 3 H); IR (neat) 1715 (C=O), 1565, 1440, 1410, 1350, 1320, 1220, 1155, 1140, 1080, 1015, 790, 770, 735, 710 cm^{-1}; MS *m*/*z* 182 (M$^+$, 2), 147 (38), 141 (16), 139 (42), 105 (12), 103 (15), 77 (17); M_r calcd for $C_{10}H_{11}ClO$ 182.0498, found (MS) 182.0493.

(b) A solution of 3-bromo-2-methoxypropene (12.6 g, 83.1 mmol) in benzene was added to a solution of the mono-Grignard reagent[15] prepared from 2,6-dichlorotoluene (23.8 g, 148 mmol) in dry THF at 0 °C. The reaction mixture was then stirred at room temperature for 18 h. The mixture was then hydrolyzed with H_2SO_4/H_2O (1:1) until all solids dissolved. It was then extracted with dichloromethane. The organic layer was washed, dried, and evaporated to give the intermediate product **21**. This was hydrolyzed by stirring in 1 N HCl for 1 h. The reaction mixture was then extracted with dichloromethane, washed, dried, and evaporated. The crude product was chromatographed on silica gel using dichloromethane/hexane (1:1) as eluent to give the ketone **19**: 8.8 g (58%), identical (^{1}H NMR, IR, MS) to the previously obtained sample.

3,4-Bis(3-chloro-2-methylphenyl)hexane-2,5-dione (22). Activated MnO_2 (0.85 g, 9.78 mmol) was added to a solution of **19** (3.00 g, 16.4 mmol) in acetic acid (10 mL). The reaction mixture was heated at 120 °C for 5 h and then treated with water and extracted with dichloromethane. The organic layer was washed, dried, and evaporated. The residue was chromatographed on silica gel using dichloromethane/hexane (1:1) as eluent. Eluted first was the diketone **22**: 0.53 g (18%). Recrystallization from benzene and hexane gave colorless crystals of **22**: mp 246−248 °C; ^{1}H NMR δ 7.1−7.4 (m, 6 H), 4.95 (s, 2 H), 2.76 (s, 6 H), 1.84 (s, 6 H); IR (KBr) 3060, 2990, 2905, 1700 (C=O), 1560, 1460, 1350, 1290, 1260, 1200, 1170, 1140, 1120, 1000, 950, 845, 770, 710, 660, 625 cm^{-1}; MS *m*/*z* 362 (M$^+$, 8), 342 (20), 318 (57), 301 (85), 276 (67), 266 (28), 180 (47), 138 (49), 114 (20). Anal. Calcd for $C_{20}H_{20}Cl_2O_2$: C, 66.13; H, 5.55. Found: C, 66.15; H, 5.55.

Eluted next was colorless crystals of the furan **16**: 0.25 g (9%); mp 54−56 °C; ^{1}H NMR δ 6.8−7.3 (m, 6 H), 2.16 (s, 3 H), 2.15 (s, 3 H), 2.09 (s, 6 H); IR (KBr) 3060, 2950, 2920, 2850, 1600, 1555, 1455, 1430, 1375, 1255, 1215, 1180, 1140, 1125, 1070, 985, 850, 780, 755, 720, 690 cm^{-1}; MS *m*/*z* 344 (M$^+$, 100), 329 (14), 310 (12), 215 (19), 125 (15); M_r calcd for $C_{20}H_{18}Cl_2O$ 344.0735, found (MS) 344.0735.

3,4-Bis(3-chloro-2-methylphenyl)-2,5-dimethylfuran (16). A solution of the diketone **22** (7.00 g, 19.3 mmol) in dry THF (100 mL) and ethanol (12 mL) was added dropwise to phosphorus pentoxide (32.9 g, 232 mmol) and cooled in an ice bath. After the addition, the reaction mixture was brought to reflux, heated for 1 h, and filtered. The residue was thoroughly washed with dichloromethane. The organic fractions were combined, washed, dried, and evaporated. The crude product was chromatographed on silica gel using dichlo-

romethane/hexane (1:3) as eluent to afford **16**: 4.80 g (72%), identical (^{1}H NMR, IR, MS) to the previously obtained sample.

3,4-Bis(3-cyano-2-methylphenyl)-2,5-dimethylfuran (23).[34] This was obtained, after recrystallization from benzene and hexane, as colorless crystals (74%): mp 118−120 °C; ^{1}H NMR δ 7.1−7.6 (m, 6 H), 2.21 (s, 6 H), 2.11(s, 6 H); IR (KBr) 2940, 2905, 2840, 2205 (C≡N), 1600, 1460, 1430, 1370, 1260, 1210, 985, 920, 810, 795, 740 cm^{-1}; MS *m*/*z* 326 (M$^+$, 100), 311 (18), 283 (20); M_r calcd for $C_2H_{18}N_2O$ 326.1419, found (MS) 326.1425.

3,4-Bis(3-formyl-2-methylphenyl)-2,5-dimethylfuran (24).[34] This was obtained, after recrystallization from benzene and hexane, as colorless crystals (96%): mp 140−142 °C; ^{1}H NMR δ 10.22 (s, 2 H), 7.2−7.7 (m, 6 H), 2.39 (s, 6 H), 2.18 (s, 3 H), 2.17 (s, 3 H); IR (KBr) 3240, 3180, 3120, 3080, 2950, 2910, 2850, 2750, 1675 (C═O), 1575, 1460, 1440, 1400, 1375, 1320, 1280, 1260, 1240, 1180, 1110, 1045, 990, 790, 715, 675 cm^{-1}; MS *m*/*z* 332 (M$^+$, 100), 317 (18), 289 (14), 202 (8). Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.18; H, 5.93.

3,4-Bis[3-(hydroxymethyl)-2-methyphenyl]-2,5-dimethylfuran (25).[34] This was obtained, after recrystallization from benzene, as colorless crystals (90%): mp 178−180 °C; ^{1}H NMR δ 7.0−7.4 (m, 6 H), 4.58, 4.55 (s, 1.2:1.0 total 4 H), 2.16, 2.17 (s, ratio 1.2:1.0, total 6 H), 1.95, 2.04 (s, ratio 1.2:1, total 6 H), 1.64 (br s, 2 H); IR (KBr) 3360 (OH), 3075, 2920, 2875, 1600, 1440, 1375, 1260, 1218, 1170, 1090, 795, 760, 730, 650 cm^{-1}; MS *m*/*z* 336 (M$^+$, 100), 321 (7), 303 (8), 275 (14), 245 (14), 215 (13); M_r calcd for $C_{22}H_{24}O_3$ 336.1725, found (MS) 336.1739.

3,4-Bis[3-(bromomethyl)-2-methylphenyl]-2,5-dimethylfuran (26).[34] This was obtained, after chromatography, as colorless crystals (91%): mp 156−158 °C; ^{1}H NMR δ 6.9−7.3 (m, 6 H), 4.42, 4.44 (s, ratio 1.2:1, total 4 H), 2.18 (s, 6 H), 2.02, 2.11 (s, ratio 1.2:1.0, total 6 H); IR (KBr) 2910, 1597, 1430, 1370, 1250, 1203, 980, 923, 790, 720 cm^{-1}; MS *m*/*z* 463 (M$^+$, 52), 462 (100), 460 (50), 383 (84), 381 (80), 259 (41), 229 (31), 151 (49). Anal. Calcd for $C_{22}H_{22}Br_2O$: C, 57.17; H, 4.80. Found: C, 57.21; H, 4.80.

***anti*-8,16,2′,5′-Tetramethyl-1-thia[3.2]metacyclo[9,10-*c*]furan (27a).** A solution of **26** (1.05 g, 2.27 mmol) in benzene (200 mL) and a solution of 95% sodium sulfide nonahydrate (0.57 g, 2.27 mmol) in 95% ethanol/water (9:1; 200 mL) were added, in separate rotaflow dropping funnels, dropwise at the same rate into vigorously stirred 95% ethanol (1000 mL) under nitrogen over a period of 6 h. After the addition, the mixture was stirred for another 15 h, and the bulk of the solvent was then removed under reduced pressure. The residue was extracted with dichloromethane. The organic layer was washed, dried, and evaporated. The crude product was chromatographed on silica gel using dichloromethane/hexane (1:2) as eluent to give **27a**: 0.50 g (66%). Recrystallization from benzene and hexane gave colorless crystals of **27a**: mp 234−236 °C; ^{1}H NMR δ 7.0−7.4 (m, 6 H), 3.79, 3.67 (AB q, 4 H, J = 12.9 Hz), 2.47 (s, 6 H), 0.67 (s, 6 H); IR (KBr) 2980, 2905, 1600, 1460, 1430, 1370, 1250, 1200, 1155, 1083, 988, 977, 920, 860, 780, 760, 720, 635 cm^{-1}; MS *m*/*z* 332 (M$^+$, 100), 299 (24), 285 (12), 283 (12), 255 (22), 241 (13), 240 (10). Anal. Calcd for $C_{22}H_{22}OS$: C, 79.00; H, 6.63. Found: C, 79.10; H, 6.48.

***anti*-8,16,2′,5′-Tetramethyl-1-(methylsulfanyl)[2.2]metacyclo[9,10-*c*]furan (29).** A solution of *n*-butyllithium in hexane (0.90 mmol) was added dropwise to a solution of the thiacyclophane **27a** (0.15 g, 0.45 mmol) in dry THF (30 mL) under nitrogen at 0 °C for 20 min. Methyl iodide (1.5 mmol in 1 mL of THF) was added, until the purple color was discharged. Water and dichloromethane were added and the organic layer was washed, dried, and evaporated. The crude product was chromatographed on silica gel using dichloromethane/hexane (1:2) as eluent to yield colorless crystals of **29**: 0.15 g, (96%); mp 196−198 °C; ^{1}H NMR δ 7.0−7.8 (m, 6 H), 3.80 (dd, 1 H, J = 2.9, 3.2 Hz), 3.14 (t,, 1 H, J = 2.9 Hz), 2.58 (dd, 1 H, J = 2.9, 3.2 Hz), 2.51 (s, 6 H), 2.14 (s, 3 H), 0.54 (s, 6 H); IR (KBr) 2907, 1600, 1420, 1375, 1250, 1205, 995, 925, 795, 750, 710 cm^{-1}; MS *m*/*z* 348 (M$^+$, 70), 333 (15), 301 (30), 286 (38), 285 (100), 271 (29), 226 (14); M_r calcd for $C_{23}H_{24}SO$ 348.1547, found (MS) 348.1541.

***anti*-8,16,2′,5′-Tetramethyl[2.2]metacyclo[9,10-*c*]furan-1-ene (15b).** A solution of **29** (0.15 g, 0.43 mmol) in dichloromethane (5 mL) was added to a stirred suspension of dimethoxycarbonium fluoroborate (0.14 g, 0.86 mmol) in dichloromethane (5 mL) at −30 °C under nitrogen. After the addition, the reaction mixture was stirred without cooling for 2 h. Ethyl acetate (10 mL) was then added and the mixture stirred for another 30 min. The crystals formed were filtered to yield the salt **30**: 0.10 g (64%); mp > 300 °C.

Potassium *tert*-butoxide (60 mg, 0.53 mmol) was added to a suspension of the salt **30** (100 mg, 0.27 mmol) in dry THF (10 mL) at room temperature. The reaction mixture was stirred for 20 min and then decomposed with water and extracted with ether. The organic layer was washed, dried, and evaporated. The crude product was chromatographed on silica gel using cyclohexane as eluent to give colorless crystals of **15b**: 79 mg (96%); mp 135−137 °C; ^{1}H NMR δ 6.62−8.5 (m, 6 H), 6.16 (s, 2 H), 2.30 (s, 6 H), 1.38 (s, 6 H); IR (KBr) 3000, 2940, 2905, 1600, 1443, 1370, 1245, 1200, 1068, 978, 920, 885, 820, 788, 743, 726, 665, 625 cm^{-1}; MS *m*/*z* 300 (M$^+$, 14), 285 (100), 270 (75), 226 (32). Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.70; H, 6.70.

Photochemical Valence Isomerization of 15b To Give 14b. A solution of **15b** in benzene (5 mL) in a quartz cell was irradiated with UV light at 254 nm for 20 min. A dark purple solution was obtained. The solvent was rapidly removed, and the sample contained a mixture of **14b** and **15b**: ^{1}H NMR δ 6.2−8.5 (m, 6 H), 6.16 (s, 2 H), 2.30, 2.38 (s, ratio 2.0:1.0, total 6 H), 1.38, 0.30 (s, ratio 2.0:1.0, total 6 H); UV/vis (cyclohexane) λ_{max} 218 (sh), 230, 278, 291, 318, 353, 370, 540, 586 nm.

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(34) For the general conditions of the series of reactions involving Cl → CN → CHO → CH_2OH → CH_2Br, refer to refs 14 and 22.