Conjugated and Cross-Conjugated π-Extended Cycloproparenes with Dithiole and Cyclopentadiene Functionality

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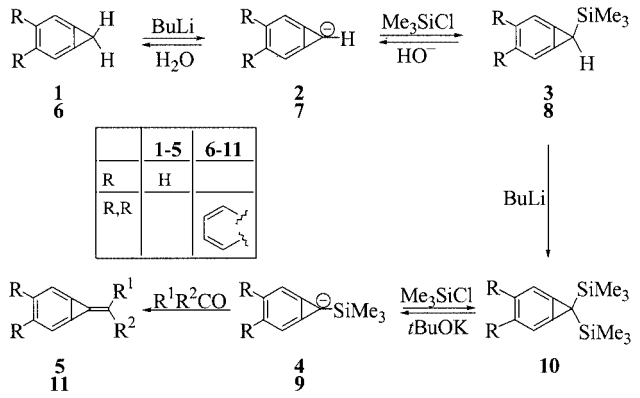
Dithiole and cyclopentadiene rings have been introduced into functionalised cyclopropa[*b*]naphthalenes to provide highly coloured, conjugated and cross-conjugated π-extended derivatives that have varying stability. Cyclopentadienylidene-containing cyclopropanaphthalene **18** and its dithiolylidene analogue **25** are prepared from bromophenylcyclopropanaphthalene **12**, and the 1,1-biscyclopentadienylidene **20** from dibromide **13**. Use of dithiole-containing ketones with 1,1-bis(trimethylsilyl)cyclopropa[*b*]naphthalene **10** gives the π-extended cycloproparenes **27** and **29** in Peterson olefinations that are more efficient than Wittig–Horner reactions of cyclopropanthraquinone **31** with dithiolate **24** to give the cross-conjugated cycloproparenes **34** and **35**.

Introduction

The class of strained aromatic hydrocarbons known as the cycloproparenes, and illustrated by parent 1*H*-cyclopropabenzene **1** has provided much fascinating chemistry[1] since Anet and Anet[2] reported the first authenticated derivative in 1964. The benzylic nature of the C1 protons, with a measured[3] pK_a for **1** (ca. 36) has led to use[4] of the C1 cycloproparenyl anion (e.g. **2**) in routine syntheses to give exocyclic alkenes (e.g. **5**) from Peterson olefinations (Scheme 1).[5−8] Because of the notable malodour of volatile **1**, the bulk of the studies have employed crystalline cyclopropa[*b*]naphthalene **6** to provide a wide range of examples[1] (e.g. **11**) that now encompass "push-pull" derivatives,[1,7] fluorescent compounds,[6,8,9] and, with some, the ability to form charge-transfer complexes.[10] These features suggest that the cycloproparene frame could behave as a valuable template for electronic effects from inclusion of extended π-conjugation.



Scheme 1

The generation of the cyclopentadienyl anion as the electron sink in "push-pull" π-conjugated systems forms a cornerstone of physical-organic chemistry and therefore, the physical and chemical properties of tetrathiafulvene (TTF) derivatives have been extensively explored.[11] While the TTF core has been modified, particularly by way of quinonoid spacers,[12] much less attention has been devoted to compounds that carry just one dithiole unit, even though they form charge transfer (CT) complexes with comparable properties to those derived from TTF.[13] Since strained molecules incorporating modified TTF or dithioles are even rarer,[14] it became evident that the incorporation of cyclopentadiene and dithiole into cycloproparenes carrying exocyclic π-conjugation should be examined. Here, we provide details on the cyclopentadienylidene-containing cycloproparenes **18** and **20**, and the dithiole derivatives **25**, **27**, **29**, and the cross-conjugated dithioles **33** and **34**.

Results and Discussion

By employing the reaction sequence of Scheme 1, shelf-stable disilane[1,7] **10** was obtained for subsequent use. Peterson olefination of this with *p*-bromo- and *p*,*p*′-dibromobenzophenone gave the previously unknown exocyclic alkenes **12** (R^1 = *p*-BrC_6H_4, R^2 = Ph) and **13** (R^1 = R^2 = *p*-BrC_6H_4; Scheme 2) in isolated yields of 90 and 94 % as bright yellow and lustrous orange crystals, respectively. As

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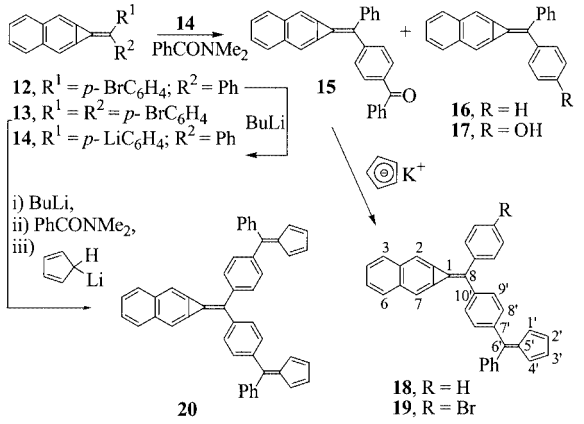
alkylidenecyclopropanes are stable to base,[1] halogen-lithium exchange is easily accomplished, and under anaerobic conditions a solution of **14** was formed from **11** and *n*BuLi. Subsequent reaction of this with *N*,*N*-dimethylbenzamide gave the benzoyl derivative **15** (77 %) together with a small amount of the known[15] un-substituted hydrocarbon **16** (Scheme 2).

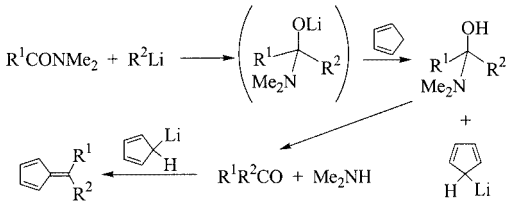


Scheme 2

The formation of **15** follows from a classical "addition-elimination" reaction between lithiate **14** and an amide-carbonyl group, while the formation of hydrocarbon **16** is consistent only with protonation of the reactive intermediate **14**, which is likely to occur during workup rather than with residual water in the reaction medium.[4] It is important that atmospheric oxygen be excluded from the reaction apparatus otherwise oxygenation of the lithiate takes place[16] with subsequent formation of the phenol **17** (20 %) that is accompanied by hydrocarbon **16** (40 %); specific aeration of a solution of lithiate **14** followed by workup affords **16** and **17** in yields of 33 and 20 %, respectively (Exp. Sect.). With the exception of reactive **14**, the structures of the alkylidenecyclopropanes **12**−**17** are assigned with confidence from their analytical and spectroscopic data. In particular, shielding of the C2(C7) carbon atoms in the ^{13}C NMR spectra matches expectation.[1] It is notable that benzoyl derivative **15** occludes dichloromethane and is hygroscopic. It forms a 2:1 complex with water which provided appropriate analytical data.

Reaction of ketone **15** with the cyclopentadienyl anion was accomplished following literature procedures[17] and produced the π-extended pentafulvalenyl cyclopropanes **18** (31 %) (Scheme 2) that also occludes solvent. The ^1H NMR spectrum shows the olefinic cyclopentadienyl protons as three distinct 1:1:2 multiplets as expected from their non-equivalence [δ = 6.32−6.34 (1H), 6.49−6.51 (1H), and 6.63−6.69 (2H) ppm]. The remote H3(H6) signal of the cyclopropanaphthalene appears as a clearly discernible two-proton AA′ multiplet, and H2(H7) reflects the facial asymmetry appearing as *para*-coupled one-proton doublets (δ = 7.59 and 7.63 ppm, J = 1.6 Hz). The ^{13}C NMR spectrum of unsymmetrical **18** is complex and displays twenty-one discernible resonances in the range δ = 107−152 ppm. Of these twelve are quaternary and C2(C7) are not differentiated but appear as a shielded[1] singlet at δ = 107.5 ppm. Unfortunately, only small "push-pull" character could be inferred from the shifts (ca. 3−4 nm) in absorption maxima on changing the UV-Vis solvent from nonpolar to polar (Exp. Sect.). Furthermore, compound **18** was obtained as a powder that did not provide crystals suitable for X-ray structural analysis.

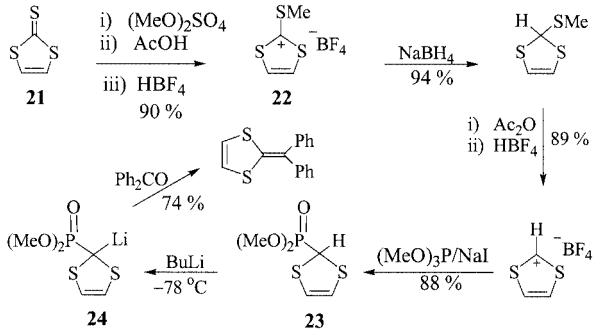
Attempts to prepare the cyclopentadiene-containing **18** and its bromine-containing homologue **19** from bromides **12** and **13**, respectively, were also devised following procedures developed by Oda et al.[18] They found that the intermediate derived from addition of an organolithium to an amide can be intercepted directly by cyclopentadiene to give a 6,6-disubstituted pentafulvalene through in situ formation of the ketone and cyclopentadienyl anion (Scheme 3). Indeed, this procedure is most efficacious because in our laboratory 6,6-diphenylpentafulvalene was prepared in good yield (65 %) from lithiation of bromobenzene followed by the addition of *N*,*N*-dimethylbenzamide and then cyclopentadiene.[18] When applied to monobromide **12**, the reaction produced a complex mixture of at least ten products from which radial chromatography afforded a red oil (R_F, 0.5) the spectroscopic data for which clearly showed the presence of **18** (vide supra); all attempts to isolate a pure sample led to product decomposition.



Scheme 3

Dibromide **13** with 1 molar equivalent of *n*BuLi (as required for the preparation of monocyclopentadiene-containing **19**) and cyclopentadiene also provided a complex mixture containing about ten components. In this case radial chromatography provided a bright orange oil (R_F, 0.5) but the ^1H NMR spectrum indicated not **19**, but the bis-cyclopentadiene derivative **20** (Scheme 2) since the H2(H7) signal appears as a distinct singlet (δ = 7.65 ppm) in a ratio of 1:1:1:2 with the three types of cyclopentadienylidene protons (δ = 6.32−6.36, 6.48−6.52, and 6.63−6.70 ppm). Attempts to purify the product resulted in significant decomposition and only after routine chromatography, separation over the size-exclusion gel Sephadex-LH-20™, and further radial chromatography could a pure sample be obtained for analysis (1 % yield). The marked sensitivity of this compound to the conditions of purification deterred us from subsequent attempts to gain further samples of it or, indeed, the search for the monocyclopentadienyl-containing analogue **19**.

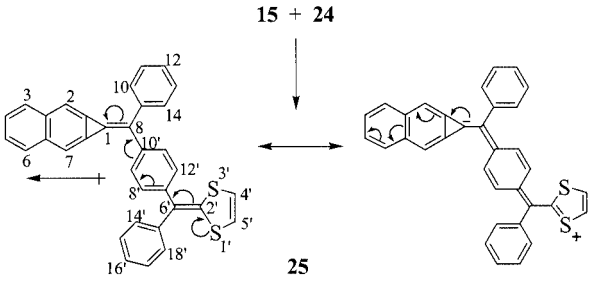
The incorporation of a dithiole moiety into an organic ketone is now achieved comparatively easily by Wittig−Horner olefination using carbanion **24** as described by Moore and Bryce.[19] This essential anion is generated readily by metallation of phosphonate ester **23** with *n*-butyllithium at low temperatures and, in turn, ester **23** is prepared from commercially available vinylene trithiocarbonate **21** (Scheme 4) in four steps through **22** in 66 % overall yield. In order to test the efficacy of the Wittig−Horner reaction with anion **24**, its reaction with benzophenone was repeated whereupon olefination was achieved in 74 % yield (Scheme 4), somewhat higher than the literature value.[19]



Scheme 4

Reaction of benzoylcycloproparene **15** with **24** likewise resulted in an efficient olefination of the carbonyl group and the novel π-extended dithiole-containing cyclopropparene **25** was isolated in 66 % yield as a bright rust coloured powder that is both light and acid sensitive; it too occludes solvent. The aromatic region of the ^{1}H NMR spectrum integrates for the twenty protons expected. Of these a single one-proton *para*-coupled doublet (δ = 7.54 ppm, J = 1.8 Hz) for H2 or H7 is clearly visible as is the two-proton AA′ component of an AA′BB′ spin system [7.86−7.90 ppm, H3(H6)]. Importantly, the two nonequivalent vinyl protons of the newly incorporated dithiole ring appear as doublets [δ = 6.24 and 6.28 ppm, J = 6.6 Hz]. The ^{13}C NMR spectrum has 25 of the expected 28 resonances distinguishable with the C2(C7) carbon atoms shielded and at δ = 107.0(6) and 107.1(6) ppm. The assigned resonances compare well with those of (diphenylmethylidene)cyclopropanaphthalene **16** but with the C1 and C3(C6) methine carbon signals slightly shifted upfield. The molecule is presumed to be stabilised by charge separation throughout as indicated in Scheme 5.

The good yield in which **25** was obtained provided sufficient material to assess its ability to act as a donor and form a CT salt with an appropriate electron acceptor. In the event, a MeCN solution of **25** gave an instantaneous colour change from red/yellow to dark green when two molar equivalents of DDQ were added. The electronic absorption spectrum of the green solution showed the absorption bands of donor **25** and acceptor DDQ to be replaced by new absorptions (Table 1). Characteristic of CT formation



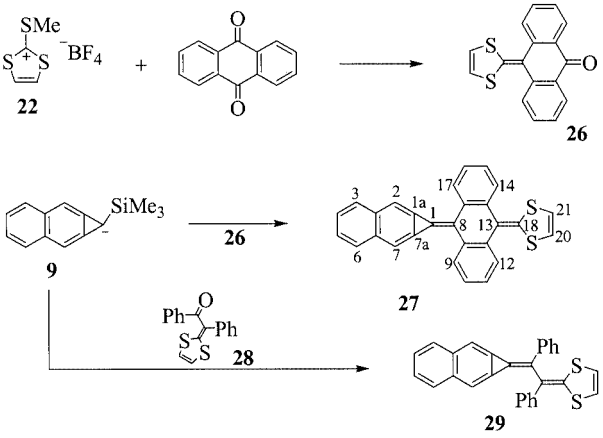
Scheme 5

Table 1. Electronic absorption data for DDQ, **25**, and **25**·DDQ (1:2); recorded at ambient temperature on a Hewlett−Packard 8452A diode-array spectrophotometer for acetonitrile solutions

Compound	λ_{max} (nm)
DDQ	272, 280, 372
25	230, 275, 294 sh, 441
25 + DDQ (1:2)	252, 347, 436, 540−620 (broad)

is the appearance of a weak long wavelength absorption[20] and, indeed **25**·DDQ (1:2) has such a broad absorption band in the range 540−620 nm, viz. at markedly longer wavelengths than the absorption maxima of the individual components. Attempts to isolate the solid CT complex were unsuccessful and decomposition took place at −16 °C overnight.

An alternative strategy for incorporating novel π-electron donors into the cyclopropparene frame would involve the Peterson olefination of α-silyl anion **9** with a carbonyl-containing compound already carrying a dithiole moiety, for example, the known[19] anthronedithiolylidene **26** to give the linear π-extended alkylidenecycloproparene **27** (Scheme 6). Synthon **26** is available from the Wittig−Horner olefination of anthraquinone by phosphonate ester **24** but it is obtained in only low (10 %) yield as the bis-adduct dominates.[19] An alternative preparation uses the dithiolium salt **22** (Scheme 4) and anthrone, which upon reflux in pyridine and acetic acid provides the sought after **26** in 85 % yield (Scheme 6).[21]

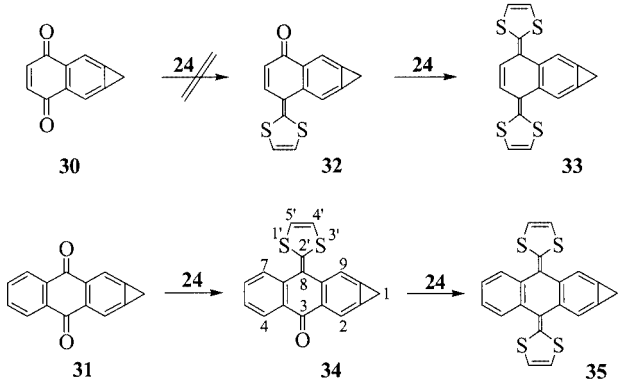


Scheme 6

Treatment of ketone **26** with anion **9** gave a complex mixture of products, the separation of which led to a red residue. This produced analytically pure dark red/black needles of the sought after alkylidenecyclopropareneene **27** carrying the anthrylidene spacer, but only in 6 % yield and this could not be improved upon in subsequent experiments. The ^{1}H NMR spectrum of **27** matches the symmetrical structure as it shows a four-proton AA′BB′ spin system [δ = 7.89−7.92 and 7.47−7.50 ppm for H3(H6)and H4(H5), respectively] with the H2(H7) and H20(H21) methine protons of the dithiole ring as two-proton singlets (δ = 7.65 and 6.28 ppm, respectively); the ^{13}C NMR spectrum displays the respective carbon atom signals at δ = 107.8 (C2 and C7) and 117.1 (C20 and C21) ppm. The low yields of **27** have precluded a detailed examination of its physicochemical properties although one flake showed packing in highly ordered sheet-like arrays from attempted single-crystal analysis. Each sheet has the molecules of **27** aligned parallel to one another with the dithiole moiety continuing the bending from the plane that contains the cyclopropareneene Adjacent sheets are stacked such that a molecule in one layer holds its neighbour in the next layer in a "ying-yang" or "fireman's grip" array, but with the molecules offset so as to maximise the S···S interactions. Although the crystal data obtained were far from an acceptable accuracy for deposition they adequately described the crystal packing present in the structure.[22] This is illustrated in Figure 1 which employs the 6−31G** energy minimised structure.

In separate experiments, the monodithiole **28** derived from 1,2-diphenylethanone was prepared, and it provided the linear π-extended cyclopropareneene **29** (Scheme 6) but, once again, the compound is available only in low (13%) yield and it is sensitive to light, acid, and the chromatographic adsorbants used in its separation. This butadiene-containing cyclopropareneene **29** is the first example of a π-extended derivative in which a simple alkene extends the conjugation.[1]

The Wittig−Horner reaction between lithiate **24** and naphthoquinone[23] **30** failed to provide any evidence for either the mono- or bis-substituted derivatives **32** and **33** (Scheme 7) despite many variations in the reaction conditions. By way of contrast, the reactions of **24** with cyclopropanthraquinone[24] **31** led to the mono- and bis(dithiole) containing cross-conjugated cyclopropanthracenes **34** (23 %) and **35** (23 %), the former from employing equimolar quantities of reagents and the latter from reaction with 2 molar equivalents of **24**. Dithiole **34** was isolated as a rust coloured powder of near analytical quality characterised from the protonated molecular ion in the APCI mass spectrum. The ^{1}H NMR spectrum is fully compatible with the structure and the influence of the dithiole ring is notable in that H2 and H9 resonate as well separated *para*-coupled doublets (δ = 8.10 and 7.81 ppm, J = 1.8 Hz), while the vinylic dithiole protons appear as a two-proton singlet (δ = 6.42 ppm). The benzylic hydrogen atoms appear as a singlet



Scheme 7

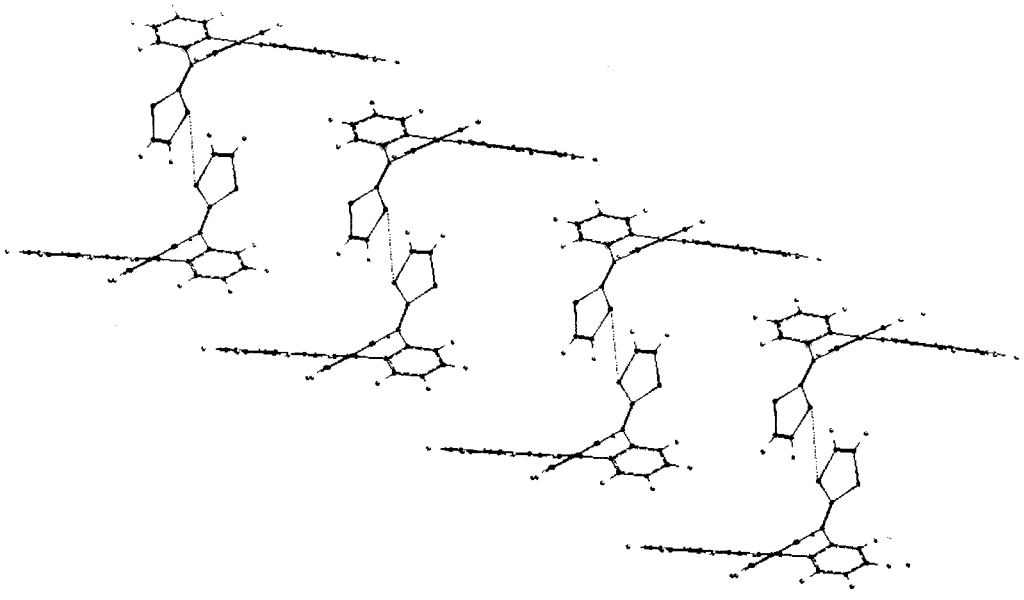


Figure 1. Packing in the sheets of dithiole **20**

(δ = 3.39 ppm) in marked contrast to homologue **35** (vide infra); the assumed nonplanar saddle-like shape[25] of **34** must be inverting rapidly in $CDCl_3$ solvent at room temperature to equate the methylene protons.

The ^{13}C NMR spectrum of cyclopropanthracene **34** also fits nicely with the assigned structure with the diagnostic C2(C9) carbon atoms adjacent to the three-membered ring shielded at δ = 113.0 and 113.8 ppm; the APCI mass spectrum provides an appropriate protonated molecular ion. Attempts were made to grow crystals of **34** suitable for an X-ray analysis and, while significant decomposition took place, a few truncated cones were obtained, but no diffraction patterns were observed.[22]

Bis(dithiole) **35** (23 %) was isolated from the reaction of **31** with two molar equivalents of **24** as an unstable yellow powder that decomposed upon attempted purification; **35** is sensitive to both acid and light. However, the ^1H NMR spectrum of the somewhat impure sample, clearly showed the expected AA′BB′ spin system (δ = 7.68−7.73, 7.29−7.32 ppm) for H3(H6) and H4(H5), and a two-proton singlet for H2(H) at δ = 7.65 ppm. The formally nonequivalent vinylic protons of the dithiole moiety are unaffected by the remote cyclopropa-fusion and resonate as a broad singlet at δ = 6.27 ppm that compares well with that in the analogous product from anthraquinone (δ = 6.30 ppm).[19] The most notable feature of the spectrum is the nonequivalence of the C1 geminal protons which resonate as a pair of one-proton doublets at δ = 3.14 and 3.60 ppm (J = 4.2 Hz). This must arise from the adoption of a nonplanar, saddle conformation in which the two 1,3-dithiole rings assume a U-shape with the bridging ring, such that the steric repulsions between the sulfur atoms and the C2(C4) and C7(C9) *peri*-hydrogen atoms of the cyclopropanthracene moiety are minimised (Figure 2).[25] In turn, this causes the nonequivalence of the C1 methylene protons, such that boat-to-boat inversion to equate hydrogen atoms (H_a and H_b) is slow in $CDCl_3$ on the NMR time scale (25 °C).

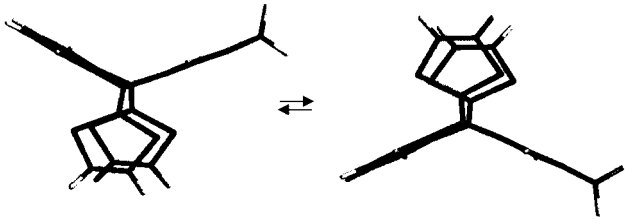


Figure 2. Minimum energy conformers of bis(dithiole) **35**

The ^{13}C NMR spectrum of **35** shows C2(C9) shielded (δ = 113.1 ppm) as expected,[1] and distinct signals for the aromatic methines C4(C7) and C5(C6) (δ = 124.8 and 125.9 ppm); the nonequivalence of the dithiole C4′ and C5′ is only just detectable [δ = 117.0(3) and 117.0(5) ppm]. These last three resonances have essentially the same chemical shifts as those in the parent anthracene analogue (δ = 124.9, 125.9, and 117.1 ppm).[19] Importantly, the APCI mass spectrum provides a protonated molecular ion (m/z = 392.9890) that confirms the composition. Unfortunately, the dithiole-containing cycloproparenes **34** and **35** decompose over 24 hours in solution, within one week in the solid state, or when left in a well-lit room. This and the low yielding syntheses have precluded any further examination of their properties.

It seems clear that a range of conjugated and cross-conjugated alkylidenecycloproparenes beyond those described here should be capable of synthesis. However, the poor product yields and the limited stability of most of the compounds described here imply that little is to be gained from such work. We are continuing our investigations upon the characteristics of specifically targeted novel π-extended cycloproparenes and will report upon these studies in due course.

Experimental Section

General: Microanalyses were performed by the Analytical Facility, Otago University, Dunedin. Mr. O. Zubkov recorded the mass spectra with high resolution coming from a PE Biosystems Mariner 5158 TOF spectrometer operating in electrospray mode, and Electron Impact (EI) 70 eV data from a Hewlett−Packard 5995C instrument. ^1H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA 300 MHz spectrometer with deuterated chloroform using the residual solvent peak as internal standard. ^{31}P NMR spectra were recorded on the same instrument using 10 % phosphoric acid in D_2O as internal standard (δ = 0.00 ppm). The usual notations define NMR multiplicities and coupling constants are in Hertz. The assignment of ^{13}C and ^1H NMR resonances was made with the aid of DEPT and ^1H-^1H COSY and ^{13}C-^1H HSQC experiments, and heteronuclear multiple-bond connectivity (HMBC) experiments. IR spectra of solid samples were recorded with KBr disks using a Biorad FTS 7 spectrophotometer while UV-Vis spectra were measured on a Hewlett−Packard 8452A diode-array spectrophotometer. Melting points were determined with a Reichert hot-stage melting point apparatus and are uncorrected. Thin-layer chromatographic analyses were performed using Merck Kieselgel (Alufoilen) $60F_{254}$ to a thickness of 0.2 mm and components detected under a UV lamp at 254 or 350 nm. Radial chromatography plates were coated with silica gel DGF_{254} to a thickness of 1, 2, 3, or 4 mm, and the total amount of material loaded onto the plate was 0.25 g, 0.75 g, 1.12 g, and 1.5 g, respectively. Column chromatography employed Kieselgel 60 (230−400 ASTM) as the stationary phase unless otherwise stated. Solvents were purified before use according to the procedures given in Perrin, Armarego, and Perrin.[26]

General Method for the Synthesis of Alkylidene-1*H*-cyclopropa[*b*]-naphthalenes: A solution of freshly sublimed potassium *tert*-butoxide (1 equiv.) in anhydrous THF (ca. 10 mL) was added dropwise by a syringe needle to a cooled solution (−70 °C) of disilane[8] **10** (1 equiv.) and the carbonyl compound (1 equiv.), in THF (ca. 10 mL) under a nitrogen atmosphere. The mixture was stirred at −70 °C for 1 h then warmed to ambient temperature overnight. The reaction was quenched (water/dichloromethane, 1:1; 50 mL) and the organic phase extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed (water; 3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a crude product that was purified as described.

1-[(*p*-Bromophenyl)phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene (12): A stirred solution of disilane **10** (284 mg, 1 mmol)[8] and *p*-bromobenzophenone (261 mg, 1 mmol) in dry THF (10 mL) gave a bright yellow oil which on trituration (hexane, −16 °C) afforded

1-[(*p*-bromophenyl)phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene (**12**). Yield 345 mg, 90 %. Bright yellow needles, m.p. 100−101 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (apparent tt, *J* = 7.3, 1.6 Hz, 1 H, 18-H), 7.44−7.51 (m, 4 H, 4-H/5-H and 17-H/19-H), 7.53−7.63 (m, 6 H, 2-H/7-H, 10-H/14-H, and 11-H/13-H), 7.70−7.74 (m, 2 H, 16-H/20-H), 7.86−7.89 (m, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.4(7) (C2 or C7), 107.6(0) (C7 or C2), 112.3 (Cl), 118.5 (C8), 121.1 (C12), 126.9(0) (C4/C5), 126.9(4) (Cla or C7a), 126.9(9) (C7a or Cla), 127.6 (C18), 128.1 (C16/C20), 128.6 (C17/C19), 128.8 (C3/C6), 129.7 (C10/C14 or C11/C13), 131.6 (C11/C13 or C10/C14), 138.5 (C9), 138.7(9) (C2a or C6a), 138.8(1) (C6a or C2a), 139.0 (C15) ppm. MS (70 eV): *m*/*z* (%) = 385 (16) [$C_{24}H_{15}{}^{81}Br$ + 1], 384 (63) [$C_{24}H_{15}{}^{81}Br$], 382 (57) [$C_{24}H_{15}{}^{79}Br$], 304 (10), 303 (37) [M − Br], 302 (100) [M − HBr], 301 (18), 300 (47), 298 (10), 151 (19), 150 (19). IR (KBr): $\tilde{\nu}$ = 3036, 3007, 1777, 1588, 1478, 1443, 1418, 1345, 1136, 1069, 1009, 841, 760, 748, 741, 698 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 230 (4.71), 276 (4.47), 292 sh (4.27), 412 (4.62), 438 nm (4.64); (acetonitrile) (log ε) λ_{max} = 230 (4.73), 273 (4.49), 288 sh (4.36), 412 (4.64), 435 nm (4.65). $C_{24}H_{15}Br$ (383.02): calcd. C 75.2, H 3.9(5), Br 20.8(5); found C 75.4, H 3.7(5), Br 20.7.

1-[Bis(*p*-bromophenyl)methylidene]-1*H*-cyclopropa[*b*]naphthalene (13): A stirred solution of **10** (500 mg, 1.76 mmol)[8] and *p*,*p*′-dibromobenzophenone (598 mg, 1.76 mmol) in THF (20 mL) gave a bright orange solid which upon trituration (hexane, −16 °C) afforded 1-[bis(*p*-bromophenyl)methylidene]-1*H*-cyclopropa[*b*]naphthalene (**13**). Yield 759 mg, 94 %. Lustrous orange crystals, m.p. 193−194 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50−7.53 (BB′, 2 H, 4-H/5-H), 7.59 (broad s, 10 H, 2-H/7-H, 9-H/13-H and 10-H/12-H), 7.89−7.93 (AA′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.8 (C2/C7), 112.6 (C1), 117.3 (C8), 121.3 (C12), 126.6 (Cla/C7a), 127.1 (C4/C5), 128.9 (C3/C6), 129.5 (C10/C14 or C11/C13), 131.7 (C11/C13 or C10/C14), 138.0 (C9), 138.9 (C2a/C6a) ppm. HRMS (positive APCI) calcd. for $C_{24}H_{15}{}^{79}Br_2$ [M + H$^+$] 460.9541; found 460.9549 (+1.74 mmu). IR (KBr): $\tilde{\nu}$ = 3046, 3034, 1777, 1482, 1423, 1392, 1346, 1248, 1176, 1136, 1071, 1005, 967, 835, 825, 751, 721, 703 cm^{-1}. UV-Vis (cyclohexane) (log ε) λ_{max} = 230 (4.68), 276 sh (4.50), 284 (4.53), 414 (4.59), 440 nm (4.60); (acetonitrile) (log ε) λ_{max} = 230 (4.68), 274 sh (4.49), 281 (4.52), 412 (4.59), 438 nm (4.59). $C_{24}H_{14}Br_2$ (462.9) calcd. C 62.4, H 3.0(5); found C 62.3, H 3.0.

1-[(*p*-Benzoylphenyl)phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene·0.85 CH_2Cl_2 (15): *n*-Butyllithium (2.30 M, 0.79 mL, 1.82 mmol) was added to a cooled (−78 °C) stirred solution of **12** (700 mg, 1.82 mmol) in dry THF (20 mL) under argon. The dark mixture was stirred and kept at this temperature for 1 h before solid *N*,*N*-dimethylbenzamide (411 mg, 1.82 mmol) was quickly added in one portion under a steady flow of dry argon. The mixture was warmed to ambient temperatures overnight, poured into water/dichloromethane (200 mL; 1:1), and the phases separated. The organic layer was washed (water, 2 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure to produce an orange oil. Radial chromatography (light petroleum elution) provided 1-diphenylmethylidene-1*H*-cyclopropa[*b*]naphthalene (**16**). Yield 68 mg, 12 %. Bright yellow oil with NMR spectroscopic data identical to those of an authentic sample.[27] Further elution (dichloromethane/light petroleum; 1:1) gave a yellow residue, recrystallisation of which (diethyl ether) provided 1-[(*p*-benzoylphenyl)phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene·0.85 CH_2Cl_2 (**15**). Yield 570 mg, 77 %. Bright yellow crystals, m.p. 76−78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (apparent tt, *J* = 7.3, 1.7 Hz, 1 H, 17-H or 25-H), 7.48−7.56 (m, 6 H), 7.60−7.65 (m, 3 H, 2-H/7-H and 17-H or 25-H), 7.75−7.79 (m, 2 H), 7.88−7.96 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.9 (C2 or C7), 108.0 (C2 or C7), 113.7 (C1), 118.5 (C8), 126.8, 127.0 (CH), 127.5 (CH), 127.6 (C17 or C25), 128.2 (CH), 128.3 (CH), 128.6 (CH), 128.9 (CH), 130.0 (CH), 130.5 (CH), 132.3 (C25 or C17), 135.3, 135.9, 137.9, 138.8, 138.9, 139.0, 143.9, 196.1 (C13) ppm. HRMS (positive APCI) calcd. for $C_{31}H_{21}O$ [M + H]$^+$ 409.1587; found 409.1565 (−5.4 mmu). IR (KBr): $\tilde{\nu}$ = 3049, 2923, 1774, 1650, 1594, 1444, 1346, 1314, 1277, 1174, 1135, 936, 923, 850, 763, 747, 698, 664 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 230 (4.99), 260 (4.93), 278 (4.95), 422 (4.81), 446 nm (4.80); (acetonitrile) (log ε) λ_{max} = 230 (5.09), 260 (4.91), 280 (4.79), 423 (4.99), 442 nm (4.97). $C_{31}H_{20}O$·0.85 CH_2Cl_2 (480.39): calcd. C 79.5, H 4.3; found C 79.0, H 4.6. Pulverising the sample and placing it under high vacuum gave hemihydrate 1-(*p*-benzoylphenyl)phenylmethylidene-1*H*-cyclopropa[*b*]naphthalene·0.5·H_2O. Yellow powder, m.p. 66−69 °C. $C_{31}H_{20}O$·0.5H_2O (417.2) calcd. C 89.2, H 5.1; found C 89.4, H, 5.0.

Preparation of 1-[(*p*-Hydroxyphenyl)phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene (17) from Lithiate 14 and Oxygen: *n*-Butyllithium (2.5 M, 0.1 mL, 0.26 mmol) was added to a stirred solution of **12** (100 mg, 0.26 mmol) in dry THF (2 mL) at −78 °C under argon. The dark mixture was stirred for 1 h then 10 mL of air was injected into the flask. After warming to ambient temperatures overnight, the mixture was poured into a mixture of water/dichloromethane (100 mL; 1:1), the phases were separated, and the organic layer was washed (water, 2 × 25 mL), dried ($MgSO_4$), and concentrated under reduced pressure to produce an orange oil. Radial chromatography (light petroleum elution) gave hydrocarbon **16**. Yield 26 mg, 33 %. Bright yellow oil with NMR spectroscopic data identical to those of the authentic sample.[27] Further elution (dichloromethane/light petroleum; 1:1) gave 1-[(*p*-hydroxyphenyl)phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene (**17**). Yield 17 mg, 20%. Dark green/brown solid, m.p. 85−88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.02 (br. s, 1 H, OH), 6.93−6.97 (m, 2 H, 11-H/13-H), 7.37 (apparent tt, *J* = 7.3, 1.7 Hz, 1 H, 18-H), 7.45−7.52 (m, 6 H, 2-H/7-H, 4-H/5-H and 17-H/19-H), 7.63−7.68 (m, 2 H, 10-H/14-H), 7.74−7.77 (m, 2 H, 16-H/20-H), 7.86−7.89 (AA′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 106.6(8) (C2 or C7), 106.7(1) (C7 or C2), 110.7 (C1), 115.4 (C11/C13), 119.6 (C8), 126.5(6) (C4/C5), 126.5(8) (C4/C5), 127.4 (C18), 127.5 (Cla/C7a), 128.2 (C16/C20), 128.4 (C17/C19), 128.7 (C3/C6), 129.6 (C10/C14), 132.1 (C9), 138.5(8) (C2a or C6a), 138.6(2) (C6a or C2a), 139.6 (C15), 155.0 (C12) ppm. HRMS (positive APCI) calcd. for $C_{24}H_{15}O$ [M − H]$^+$ 319.1137; found 319.1131 (−1.88 mmu). IR (KBr): $\tilde{\nu}$ = 3401, 2975, 2953, 1633, 1608, 1445, 1413, 1384, 1267, 1173, 1138, 1089, 1049, 880, 845, 698 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 230 (4.58), 275, (4.28), 413 (4.43), 441 nm (4.50); (acetonitrile) (log ε) λ_{max} = 230 (4.58), 274 (4.29), 275 (4.29), 414 (4.43), 440 nm (4.48).

1-[10′-(6,6-Diphenylpentafulvalenyl)]phenylmethylidene-1*H*-cyclopropa[*b*]naphthalene·0.18 C_6H_{14} (18): Cyclopentadiene (0.02 mL, 0.25 mmol) followed by freshly ground potassium hydroxide (14 mg, 0.25 mmol) was added to a stirred solution of *p*-benzoylphenylcyclopropanaphthalene·0.9 CH_2Cl_2 (**15**) (100 mg, ca. 0.83 mg unsolvated, ca. 0.20 mmol) and 18-crown-6 (4 mg, 0.01 mmol) in dry THF (10 mL) at 0 °C and under argon. The dark red mixture was stirred overnight at room temperature and poured into water/dichloromethane (100 mL; 1:1). After separating the phases the aqueous layer was extracted (dichloromethane, 2 × 25 mL), and the combined organic layers were washed (water; 2 × 25 mL), dried ($MgSO_4$) and concentrated under reduced pressure to a red oil. Radial chromatography (dichloromethane/light petro-

leum elution; 4:1) and collection of the only mobile component gave an orange oil that on trituration (dichloromethane/hexane −16 °C) gave 1-[10′-(6,6-diphenylpentafulvalenyl)]phenylmethylidene-1*H*-cyclopropa[*b*]naphthalene·0.18 C_6H_{14} (**18**). Yield 30 mg, 31 %; based on the unsolvated alkylidenecyclopropanaphthalene used. Orange powder, m.p. 122−124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.32−6.34 (m, 1 H, 1′-H or 5′-H), 6.49−6.51 (m, 1 H, 5′-H or 1′-H), 6.63−6.69 (m, 2 H, 3′-H/H4′-H), 7.40−7.53 (m, 12 H), 7.59 (d, *J* = 1.6 Hz, 1 H, 2-H or 7-H), 7.63 (d, *J* = 1.6 Hz, 1 H, 7-H or 2-H), 7.78−7.84 (m, 4 H), 7.89−7.93 (AA′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.5 (C2/C7), 112.7 (C1), 119.0 (C8), 124.3 (C5′ or C1′), 124.4 (C1′ or C5′), 126.8(4) (CH), 126.8(6) (CH), 127.0, 127.1 (CH), 127.4, 127.5 (CH), 127.7 (CH), 128.3 (CH), 128.5 (CH), 128.7(2) (CH), 128.7(9) (CH), 128.9 (C3/C6), 132.1 (C3′ or C4′), 132.2 (CH), 132.3 (C4′ or C3′), 132.5 (CH), 138.8, 138.9, 139.1, 140.1, 141.3, 143.8, 151.8 ppm. HRMS (positive APCI) calcd. for $C_{36}H_{25}$ [M + H]$^+$ 457.1951; found 457.1941 (−2.19 mmu). IR (KBr): $\tilde{\nu}$ = 3049, 2952, 2922, 1776, 1581, 1485 1442, 1360, 1325, 1137, 966, 848, 822, 696 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 232 (4.62) 256 (4.46), 280 (4.42), 346 (4.19), 431 (4.53), 448 nm (4.53); (acetonitrile) (log ε) λ_{max} = 230 (4.68), 254 (4.48), 283 (4.41), 344 (4.25), 437 rim (4.59). Attempts were made to prepare compound **18** from **12** (550 mg, 1.44 mmol) and *n*BuLi (1.92 M, 0.78 mL, 1.5 mmol) in dry THF (35 mL) with *N*,*N*-dimethylbenzamide (245 mg, 1.64 mmol) and then cyclopentadiene (0.24 mL, 2.88 mmol) according to the method of Oda et al.[18] The dark mixture was allowed to attain ambient temperatures overnight and was then poured into water/dichloromethane (400 mL; 1:1). The phases were separated and the aqueous mixture extracted (dichloromethane; 2 × 100 mL) and the combined organic layers washed (water, 100 mL), dried ($MgSO_4$) and concentrated under reduced pressure to produce a red oil. Radial chromatography (dichloromethane/light petroleum elution; 1:4) and collection of the component with R_F = 0.5 afforded a red oil that contained the title compound **18** (^{1}H NMR), vide infra. Attempts to further purify this oil by radial chromatography, trituration, sublimation, or by use of the Sephadex LH-20 size exclusion gel all resulted in decomposition. The identity of the decomposition products remains unknown.

1-{Bis[10′-(6,6-diphenylpentafulvalenyl)]methylidene}-1*H*-cyclopropa[*b*]naphthalene (20): *n*-Butyllithium (1.92 M, 0.52 mL, 1.14 mmol) was added to a stirred solution of dibromide **13** (461 mg, 1.0 mmol) in dry THF (35 mL) at −78 °C under argon, which follows the procedure outlined by Oda et al.[18] The mixture became dark yellow-brown and was stirred at −78 °C for 1 h, then *N*,*N*-dimethylbenzamide (169 mg, 1.14 mmol) was added under a stream of argon. The mixture was warmed, stirred at 0 °C for 1 h and then cyclopentadiene (0.17 mL, 2.0 mmol) added. The dark mixture was then allowed to attain ambient temperatures overnight, and was then poured into water/dichloromethane (400 mL; 1:1), and the phases separated. The aqueous mixture was extracted (dichloromethane; 2 × 100 mL) and the combined organic layers were washed (water, 100 mL), dried ($MgSO_4$) and concentrated under reduced pressure to produce an orange oil that contained in excess of ten components (TLC). Radial chromatography (dichloromethane/light petroleum elution; 1:4) and collection of the band with R_F = 0.5 afforded an impure orange solid. Recrystallisation (dichloromethane, −16 °C) followed by purification on Sephadex LH-20™ size-exclusion gel (THF elution) and one further radial chromatography (dichloromethane elution) gave **20**. Yield 6 mg, 1 %. Bright orange oil proposed as the title compound **20**, b.p. > 305 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.32−6.36 (m, 2 H, 1′-H or 4′-H), 6.48−6.52 (m, 2 H, 4′-H or 1′-H), 6.63−6.70 (m, 4 H, 2′-H/3′-H), 7.42−7.48 (m, 14 H, 8′-H/12′-H, 14′-H/18′-H, 15′-H/17′-H and 16′-H), 7.49−7.54 (BB′, 2 H, 4-H/5-H), 7.65 (s, 2 H, 2-H/7-H), 7.82−7.87 (m, 4 H, 9′-H/11′-H), 7.91−7.95 (AA′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.8 (C2/C7), 113.3 (C1), 118.4 (C8), 124.3 (C1′ or C4′), 124.5 (C4′ or C1′), 127.0(3) (C4/C5), 127.0(6) (Cla/C7a), 127.3 (C8′/C12′, C14′/C18′ or C15′/C17′), 127.7 (C9′/C11′), 128.7 (C16′), 128.9 (C3/C6), 132.1 (C2′ or C3′), 132.2 (C8′/C12′, C14′/C18′ or C15′/C17′), 132.4 (C2′ or C3′), 132.5 (C8′/C12′ or C14′/C18′ or C15′/C17′), 139.0 (C2a/C6a), 139.7 (C6′, C7′, C10′, C13′), 140.2 (C10′ or C7′), 141.3 (C6′, or C7′, or C10′, or C13′), 143.9 (C5′), 151.7 (C7′, C6′, C 10′ or C 13′) ppm. HRMS (positive APCI) calcd. for $C_{48}H_{33}$ [M + H]$^+$ 609.2577; found 609.2679 (+16.7 mmu). IR (KBr): $\tilde{\nu}$ = 3052, 2922, 1773, 1584, 1489, 1466, 1442, 1425, 1361, 1347, 1323, 1176, 1137, 1084, 1073, 1029, 1017, 997, 849, 824, 780, 745, 697 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 232 (4.83), 257 (4.65), 288 (4.59), 350 (4.51), 444 nm (4.68); (acetonitrile) (log ε) λ_{max} = 232 (4.74), 254 (4.56), 286 (4.51), 337 (4.38), 441 nm (4.58).

Dimethyl (1,3-Dithiol-2-yl)phosphonate (23): This was prepared from vinylene trithiocarbonate (see Scheme 4) as described previously.[19,28,29] The pale hygroscopic oil, which became red upon standing, is best stored under argon in the absence of light.

2-(Diphenylmethylidene)-1,3-dithiole: *n*-Butyllithium (2.5 M, 0.19 mL, 0.47 mmol) was added to a stirred solution of phosphonate ester **23** (100 mg, 0.47 mmol) in dry THF (20 mL) at −78 °C under argon. The suspension was stirred for 30 min at −78 °C and then benzophenone (86 mg, 0.47 mmol) was added dropwise in THF (1 mL) over 5 min. Warming to room temperature overnight was followed by quenching in water/dichloromethane (100 mL; 1:1). The phases were separated, the aqueous extracts (dichloromethane, 50 mL), and the combined organic layers were washed (water, 100 mL), dried ($MgSO_4$) and concentrated under reduced pressure to produce a pale yellow oil. Radial chromatography (dichloromethane elution) and collection of the major component followed by recrystallisation gave the title compound. Yield 93 mg, 74 %. Cream solid, m.p. 99−100 °C (ref.[19] 68 %, m.p. > 240 °C). The spectroscopic data were in excellent agreement with the literature values.[19]

1-{[10′-(6,6-Diphenyl-2,5-dithiapentafulvenyl)]phenylmethylidene}-1*H*-cyclopropa[*b*]naphthalene·0.25 C_6H_{14} (25): *n*-Butyllithium (1.65 M, 0.25 mL, 0.42 mmol) was added to a stirred solution of phosphonate ester **23** (88 mg, 0.42 mmol) in dry THF (2 mL), at −78 °C under argon. The suspension was stirred for 30 min at this temperature and then **20** (in CH_2Cl_2, 170 mg, 0.45 mmol) was added dropwise in THF (4 mL) over 5 min. The dark red mixture was warmed to room temperature overnight and then poured into water/dichloromethane (200 mL; 1:1). The phases were separated, the aqueous phase extracted (dichloromethane, 100 mL), and the combined organic layers washed (water, 100 mL), dried ($MgSO_4$) and concentrated under reduced pressure to produce a red/orange oil. Column chromatography (basic alumina, dichloromethane/hexane, 1:4, elution) gave an analytical sample of 1-{[10′-(6,6-diphenyl-2,5-dithiapentafulvenyl)]phenylmethylidene}-1*H*-cyclopropa[*b*]naphthalene·0.25 C_6H_{14} (**25**). Yield 134 mg, 66 %. Bright red powder, m.p. 69−70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.24 (d, *J* = 6.6 Hz, 1 H, 4′-H or 5′-H), 6.28 (d, *J* = 6.6 Hz, 1 H, 4′-H or 5′-H), 7.28−7.50 (m, 10 H), 7.54 (d, *J* = 1.8 Hz, 1 H, 2-H or 7-H), 7.58 (d, *J* = 1.8 Hz, 1 H, 7-H or 2-H), 7.70−7.78 (m, 4 H), 7.86−7.90 (AA′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.0(6) (C2 or C7), 107.1(6) (C7 or C2), 111.8 (C1), 117.4 (C4′ or C5′), 117.6 (C5′ or C4′), 119.5 (C8), 124.6, 126.7 (C4/C5), 127.2 (CH), 127.4 (CH), 127.6, 127.9 (CH), 128.1 (CH), 128.3(5)

(CH), 128.4(3) (CH), 128.7(0) (C3 or C6), 128.7(2) (C6 or C3), 128.9 (CH), 136.5, 137.4, 138.7, 138.8, 139.3, 140.9, 142.8 ppm. HRMS (positive APCI) calcd. for $C_{34}H_{23}S_2$ $[M + H]^+$ 495.1236; found 495.1249 (+2.6 mmu). IR (KBr): $\tilde{\nu}$ = 3048, 2951, 1773, 1593, 1487, 1442, 1419, 1345, 1135, 1029, 845, 799, 748, 697 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 230 (4.77), 278 (4.47), 292 sh (4.42), 396 sh (4.35), 449 nm (4.62); (acetonitrile) (log ε) λ_{max} = 230 (4.75), 275 (4.45), 294 sh (4.41), 441 nm (4.59).

Charge-Transfer Complexation of 25 with DDQ: A solution of DDQ (18.4 mg, 0.08 mmol) in dry acetonitrile (6 mL) was added to a stirred solution of solvated **25** (20 mg, 0.04 mmol) in MeCN (6 mL). The initially red coloured solution developed a dark green colouration: UV-Vis (acetonitrile) (log ε) λ_{max} = 252 (4.56), 282 (4.07), 294 (4.04), 312 (4.03), 347 (4.07), 436 (3.88), 540−620 nm (3.34). All attempts to isolate a crystalline product were unsuccessful and the mixture become brown, even upon standing in the freezer for 16 h.

10-(1,3-Dithiol-2-ylidene)anthracene-9(10*H*)one (26): Glacial acetic acid (10 mL, 174.7 mmol) followed by pyridine (2 mL, 24.7 mmol) was added to a mixture of salt **22** (1 g, 4.24 mmol) and anthrone (0.82 mmol) under argon. The mixture was then stirred under reflux for 30 min, cooled, and the orange precipitate filtered off. The solid was washed (water, 5 × 40 mL), dried in vacuo, and recrystallised (dichloromethane) to give the title compound **26**. Yield 940 mg, 79% (ref.[21] 85 %). Bright orange needles, m.p. 220−221 °C (ref.[21] 219−221 °C). The ^1H NMR spectroscopic data were in agreement with those reported.[21] ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.1, 117.1 (CH), 124.9 (CH), 125.9 (CH), 126.1 (CH), 129.7, 130.9 (CH), 138.5, 145.0, 182.7 ppm.

9-(1*H*-Cyclopropa[*b*]naphthalene-l-ylidene)-10-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (27): Potassium *tert*-butoxide (40 mg, 0.34 mmol) in dry THF (3 mL) was added dropwise over 5 min. to a stirred suspension of dithiole **26** (96 mg, 0.34 mmol) and **10** (100 mg, 0.34 mmol) in the same solvent (15 mL) at −78 °C under argon The dark red mixture was then allowed to warm to room temperature overnight and then poured into water/dichloromethane (200 mL; 1:1). The phases were separated, the aqueous extracted (dichloromethane, 100 mL), and the combined organic layers were washed (water, 100 mL), dried ($MgSO_4$) and concentrated under reduced pressure to produce a dark red oil. Column chromatography (basic alumina, dichloromethane elution) and trituration (dichloromethane) gave 9-(1*H*-cyclopropa[*b*]naphthalene-l-ylidene)-10-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**27**). Yield 8.9 mg, 6 %. Red/black needles, m.p. 253−254 °C (the sample darkened at 111−112 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.28 (s, 2 H, 20-H/21-H), 7.40−7.44 (m, 4 H, 10-H/11-H/15-H/16-H), 7.47−7.50 (BB′, 2 H, 4-H/5-H), 7.65 (s, 2 H, 2-H/7-H), 7.76−7.78 (m, 2 H, 12-H/14-H), 7.89−7.92 (AA′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.9 (C2/C7), 109.7 (C1), 113.6 (C8), 117.1 (C20/C21), 122.3 (C13), 123.5 (C9/C17), 126.0 (C12/C14), 126.4 (C10/C16 or C11/C15), 126.7(0) (C11/C15 or C10/C16), 126.7(2) (Cla/C7a), 126.9 (C4/C5), 128.7 (C3/C6), 132.9 (C8a/C17a or C12a/C13a), 135.0 (C12/C13a or C8a/C17a), 136.8 (C18), 139.1 (C2a/C6a) ppm. HRMS (positive APCI) calcd. for $C_{28}H_{17}S_2$ $[M + H]^+$ 417.0766; found 417.0760 (−1.44 mmu). IR (KBr): $\tilde{\nu}$ = 3057, 1631, 1497, 1442, 1416, 1142, 1115, 752, 742 cm^{-1}. UV-Vis (acetonitrile) (log ε) λ_{max} = 236 (4.59), 268 (3.95), 295 sh (3.89), 382 (3.98), 420 (4.07), 508 nm (4.18). Further attempts to prepare **27** afforded yields of 3−6 %.

(2-Benzoyl)phenylmethylidene-1,3-dithiole (28): Glacial acetic acid (5 mL, 87.4 mmol) and pyridine (1 mL, 12.4 mmol) were added sequentially to a mixture of salt **22** (500 mg, 2.11 mmol) and 1,2-diphenylethanone (416 mg, 2.11 mmol) under argon. The mixture was then stirred under reflux for 45 min, cooled, and poured into water/dichloromethane (200 mL; 1:1). The phases were separated, the aqueous extracted (dichloromethane, 3 × 40 mL), and the combined organic layers were washed (water, 200 mL), dried ($MgSO_4$) and concentrated under reduced pressure to produce a brown oil that contained (from ^1H NMR examination) a 1:1 mixture of unchanged ethanone and compound **28**. The residue was then dissolved in acetic acid (5 mL) and additional salt **22** (213 mg, 1.06 mmol) added followed by pyridine (0.5 mL). Reflux with stirring for 45 min was followed by cooling with workup as described above, and the resultant was purified by column chromatography (ethyl acetate elution) to give a yellow/brown solid. Recrystallisation (THF/hexane; 1:1, −16 °C) gave the title compound **28**. Yield 575 mg, 90 % (based upon ketone used). Lustrous yellow crystals, m.p. 134−136 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.80 (d, *J* = 6.7 Hz, 1 H, 4-H or 5-H), 7.00 (d, *J* = 6.7 Hz, 1 H, 5-H or 4-H), 7.11−7.17 (m, 2 H), 7.22−7.39 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 118.9 (C4 or C5), 121.3, 125.4 (C5 or C4), 127.4 (CH), 127.9 (CH), 129.0 (CH), 129.3 (CH), 129.8 (CH), 130.3 (CH), 139.3, 140.0, 167.8, 185.8 (C8) ppm. HRMS (positive APCI) calcd. for $C_{17}H_{13}OS_2$ $[M + H]^+$ 297.0402; found 297.0395 (−2.36 mmu). IR (KBr): $\tilde{\nu}$ = 3095, 3068, 1597, 1584, 1564, 1545, 1443, 1413, 1386, 1330, 1305, 1263, 1072, 989, 741, 698 cm^{-1}. UV/Vis (acetonitrile) (log ε) λ_{max} = 231 (4.13), 250 (3.88), 400 nm (4.39). $C_{17}H_{12}OS_2$ (296.2): calcd C 68.9, H 4.1; found C 68.7, H, 4.0.

1-[1,2-Diphenyl-2-(1,3-dithiol-2-ylidene)ethylidene]-1*H*-cyclopropa[*b*]naphthalene (29): Employing ketone **28** (156 mg, 0.52 mmol) and disilane **10** (150 mg, 0.52 mmol) and following the general procedure given above, a dark red/orange oil was obtained. Column chromatography (basic alumina, dichloromethane/light petroleum elution; 4:1) afforded 1-[1,2-diphenyl-2-(1,3-dithiol-2-ylidene)ethylidene]-1*H*-cyclopropa[*b*]naphthalene (**29**). Yield 28.5 mg, 13 %. A red oil was isolated. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.26 (d, *J* = 6.7 Hz, 1 H, 18-H or 19-H), 6.31 (d, *J* = 6.7 Hz, 1 H, 19-H or 18-H), 7.16−7.45 (m, 9 H), 7.57−7.60 (m, 2 H, 10-H/14-H or 22-H/26-H), 7.68 (d, *J* = 1.6 Hz, 1 H, 2-H or 7-H), 7.82−7.93 (m, 4 H, 3-H/6-H and 10-H/14-H or 22-H/26-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.7 (C2 or C7), 109.0 (C7 or C2), 112.6 (C1), 116.9 (C18 or C19), 119.5 (C19 or C18), 120.6, 121.8, 126.5 (CH), 126.6(8) (CH), 126.7(1) (CH), 127.1 (CH), 127.4, 127.7, 128.1 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 137.5, 138.7, 138.9, 141.2 ppm. HRMS (positive APCI) calcd. for $C_{28}H_{19}S_2$ $[M + H]^+$ 419.0923; found 419.0925 (+0.48 mmu). IR (KBr): $\tilde{\nu}_{max}$ 3048, 1765, 1630, 1592, 1542, 1486, 1439, 1413, 1344, 1144, 905, 845, 760, 744, 727, 692 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 230 (4.69), 290 (4.33), 380 (4.24), 428 (3.99), 474 (4.18), 502 nm (4.21); (acetonitrile) (log ε) λ_{max} = 232 (4.65), 288 (4.31), 378 (4.22), 422 (3.99), 476 nm (4.02).

Attempted Preparation of 3,6-Bis(1,3-dithiol-2-ylidene)-3,6-dihydro-1*H*-cyclopropa[*b*]naphthalene (33): Attempts to effect reaction between 1 or 2 mol. equiv. of cyclopropanaphthoquinone[23] **30** and dithiole **24** (250 mg, 1.18 mmol) afforded a dark green solution which transformed upon work up to produce a viscous red oil containing a complex mixture of components. The ^1H NMR spectrum and TLC showed no signals which corresponded to either **30**, **24** (or, **23**), or dithioles **32** or **33**. Attempts to purify the mixture and identify its components were unsuccessful.

8-(1,3-Dithiol-2-ylidene)-3,8-dihydro-1*H*-cyclopropa[*b*]anthracene-3(8*H*)-one (34): *n*-Butyllithium (1.65 M, 0.55 mL, 0.90 mmol) was added to a stirred solution of phosphonyl **24** (193 mg, 0.90 mmol)

in dry THF (3 mL) −78 °C under argon. After stirring the suspension for 30 min anthracenedione[24] **31** was added (100 mg, 0.45 mmol) dropwise in THF (3 mL) over 5 min. The coloured mixture was warmed to room temperature overnight and poured into water/dichloromethane (200 mL; 1:1). The phases were separated, the aqueous extracted (dichloromethane, 100 mL), and the combined organic layers were washed (water, 100 mL), dried ($MgSO_4$) and concentrated under reduced pressure to produce a red/orange oil. Column chromatography (basic alumina, dichloromethane/light petroleum elution; 4:1) gave a red solid as a near analytical sample of 8(1,3-dithiol-2-ylidene)-3,8-dihydro-1*H*-cyclopropa[*b*]-anthracene-3(8*H*)-one (**34**). Yield 40 mg, 23 %. Rust coloured powder, m.p. > 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.39 (s, 2 H, 1-H), 6.42 (broad s, 2 H, 4′-H/5′-H), 7.38−7.43 (m, 1 H, 6-H), 7.59−7.65 (m, 1 H, 5-H), 7.81 (d, *J* = 1.8 Hz, 1 H, 9-H), 7.80−7.92 (m, 1 H, 7-H), 8.10 (d, *J* = 1.8 Hz, 1 H, 2-H), 8.24−8.27 (m, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.8 (C1), 113.0 (C9), 113.8 (C2), 117.8, 117.9 (C4′ or C5′), 118.0 (C5′ or C4′), 125.3, 125.8 (C7), 126.4 (C6), 126.9 (C4), 130.6, 130.9, 131.5 (C5), 133.0, 139.9, 142.7, 145.7, 183.6 (C3) ppm. HRMS (positive APCI) calcd. for $C_{18}H_{11}S_2O$ $[M + H]^+$ 307.0246; found 307.0253 (+2.3 mmu). IR (KBr): $\tilde{\nu}$ = 3093, 3059, 2926, 2852, 1636, 1594, 1573, 1479, 1443, 1285, 1231, 1123, 1099, 759, 688 cm^{-1}. UV-Vis (hexane) (log ε) λ_{max} = 251 (4.00), 358 (3.34), 431 (3.56), 451 nm (3.64); (acetonitrile) (log ε) λ_{max} = 252 (4.57), 365 (3.89), 467 nm, (4.14). Recrystallisation (dichloromethane/hexane; 1:1, −16 °C) resulted in significant decomposition and < 1 mg of truncated rust coloured cones were obtained.

3,8-Bis(1,3-dithiol-2-ylidene)-3,8-dihydro-1*H*-cyclopropa[*b*]-anthracene (35): *n*-Butyllithium (1.65 M, 0.41 mL, 0.68 mmol) was added to a stirred solution of phosphonyl **24** (145 mg, 0.68 mmol) in dry THF (5 mL) at −78 °C under argon. The suspension was stirred for 30 min and dione[24] **31** (150 mg, 0.68 mmol) was added dropwise in THF (4 mL) over 5 min. The mixture was then allowed to warm to room temperature overnight, poured into water/dichloromethane (200 mL; 1:1) and the phases separated. The aqueous phase was extracted (dichloromethane, 100 mL) and the combined organic layers were washed (water, 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to produce a red/orange oil. Column chromatography (basic alumina, dichloromethane/light petroleum elution; 4:1) gave a yellow solid that contained predominately 3,8-bis(1,3-dithiol-2-ylidene)-3,8-dihydro-1*H*-cyclopropa[*b*]anthracene (**35**). Yield 49 mg, 23 %. The compound decomposed upon further attempted purification (chromatography or recrystallisation). ^{1}H NMR (300 MHz, $CDCl_3$) data abstracted from the crude product for **35**: δ = 3.14 (d, *J* = 4.2 Hz, 1 H, H-1), 3.60 (d, *J* = 4.2 Hz. 1 H, H-1), 6.27 (broad s, 4 H, 4′-H/5′-H/9′-H/10′-H), 7.29−7.32 (BB′, 2 H, 5-H/6-H), 7.65 (s, 2 H, 2-H/9-H), 7.68−7.73 (AA′, 2 H, 4-H/7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) data abstracted from the crude product for **35**: δ = 21.0 (C1), 113.1 (C2/C9), 117.0(3) (C4′/C9′ or C5′/C10′), 117.0(5) (C5′/C10′ or C4′/C9′), 124.8 (C4/C7), 125.9 (C5/C6) ppm. HRMS (positive APCI) calcd. for $C_{21}H_{13}S_4$ $[M + H]^+$ 392.9895; found 392.9890 (−1.3 mmu).

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